THE W.K.B. APPROXIMATION FOR THE QUANTUM RADIAL DISTRIBUTION FUNCTION

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

April, 1966

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1966

DEDICATION

이 博士學位論文을
어머님과 아버님의
靈前에 올림

全鐘國 올림

(Dedicated to the Memory of my
Beloved Mother and Father)

ACKNOWLEDGMENTS

On completion of this dissertation, I gratefully acknowledge the help and advice which I have received from many quarters.

First of all I want to express my very deep gratitude to Prof. Arthur A. Broyles, my major professor; for his many suggestions and instructive discussions related to the problems which arose during the course of writing this dissertation and for reading the manuscript and his careful correction of the wrong parts, and especially in eliminating the worst Koreanisms. My thanks are also due to the following: Dr. Charles F. Hooper, a member of my supervisory committee, for reading the manuscript and correcting the wrong parts, and to Prof. Stanley S. Ballard, Chairman of the Department of Physics, to Dr. Thomas A. Scott, Dr. Billy S. Thomas, and Dr. Charles B. Smith, i.e. the other three members of my supervisory committee, for their warm-hearted assistance throughout my graduate studies.

I am particularly grateful to Dr. Lyun Joon Kim, the president and to all the faculty members of Hanyang University, i.e. my home university in Seoul, Korea, for their hearty assistance extended to my family who have remained in Seoul, Korea, and also to my wife, Mrs. Jung Im Lee, for her supporting my family in Seoul, Korea, by herself and offering her constant encouragement, and unbounded patience during my graduate study in the foreign country of the United States of America farthest from my native country of Korea.

Finally, I am grateful to Mr. R. A. Smith and Mr. C. V. Gardiner for their carrying out the complicated and tedious Fortran programs on the IBM 709 Computer related to this dissertation, and to Mr. G. Scheffer for his artful execution of the graphic work, and also to Mrs. Philamena Pearl for her typing excellently the vast pages of my manuscript involving many long mathematical expressions with complicated indices.

The author believes deeply that his graduate study leading to the Ph.D. degree could not have been achieved without all of the warm-hearted assistance of the above people.

PREFACE

This is the fifth dissertation written by a member of the statistical mechanics group under the program and direction of Dr. Arthur A. Broyles, Professor of Physics. The purpose, value, history, and future plan of the program can be seen from the booklet entitled "Progress Report on the Physics Department Project entitled the Equation of State of Dense Fluids" written by Professor Arthur A. Broyles (unpublished).

The theoretical part of classical statistical mechanics of the program has been studied thoroughly by the author's predecessors, i.e. Drs. H. L. Sahlin, A. A. Khan, D. D. Carley and F. Lado in their elegant ways.

The next step subsequent to their successful studies was to contemplate quantum-mechanically the problem. The tape of beginning this important and difficult task has been cut off by the author with his several colleagues. The main subject and methodology treated by him will be seen succinctly in Chapter I entitlted "Introduction". The author feels very humble and grateful that he has been very fortunate in successfully solving the problem with his limited ability. The theoretical result obtained by him is compared, for example, with the experimental result of neon quantum-fluid at four cases of temperatures and particle densities.

He feels now as follows: The field of sciences is broad and long. However, it seems that the depth of the philosophical principle

of the nature given once upon a time by the creator is rather mysteriously deep and far from the science constructed artificially by human beings. Poor is the scientific knowledge and idea of human being. The ultimate doubt is that the human being can, in the long run, detect surely enough and exactly the essential principles by which the natural world has been created ever before. At this point, he wants finally to quote the following H. Weyl's point of view with his resonance: Statistical physics, through the quantum theory, has already reached a deeper stratum of reality than is accessible to field physics; but the problem of matter is still wrapt in deepest gloom. We must state in unmistakable language that physics at its present stage can in nowise be regarded as lending support to the belief that there is a causality of physical nature which is founded on rigorously exact laws. It is yet able to follow the intelligence which has planned the world, and that the consciousness of each one of us is the center at which the One Light and Life of Truth comprehends itself in phenomena.

Jong K. Jaen

Gainesville, Florida
March, 1966

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CHAPTER I

INTRODUCTION

> —But the problem of matter is still wrapt in deepest gloom. ..., our ears have caught a few of the fundamental chords from that harmony of the spheres of which Pythagoras and Kepler once dreamed—(Herman Weyl)

This dissertation is concerned with the problem of equilibrium quantum-statistical mechanics, based on the Schrödinger-Heisenberg quantum mechanics, and the purpose is six fold:

(1) The presentation of the fundamental ideas and conceptions of the equilibrium quantum-statistical mechanics by taking advantage of the Dirac ket-bra vector description.

Standing on the Mach's point of view, viz. the Mach's principle of the economic use of the thought,* this purpose is trivial since this description leads us naturally to the correct result by means of the deductive method only under a simplified consideration, i.e. the arrival of the correct answer with the least consumption of our thought as well as the minimum introduction of necessary notations concerned with the given problem.

(2) The presentation of the natural arrival at the most basic conception of "the Neumann's statistical density operator" in quantum statistical mechanics starting from "the Born's density operator" in the Schrödinger-Heisenberg quantum

---

*E. Mach; Die Mechanik in ihre Entwicklung, Leipzig, 1883.

mechanics by introducing a new conception of "trajectory of the state vector of the system" in Hilbert space.

The presentation of this is due to the author's dissatisfaction with the obscure but correct conception of "the statistical weight" used first by Neumann himself and still used by many recent authors in formulating the Neumann's statistical density operator.

(3) The presentation of the new expansion theory of the quantum partition function and pair correlation function on the basis of the group-theoretical discussion of the symmetric group.

This theory will be developed basically by taking significant advantage of the unified property of all the elements in the same class of the symmetric group, i.e. the cyclic structures of all the elements in the same class are the same.

(4) The presentation of the new expansion theory of the exchange effective potential formally universal for all the quantum-mechanical systems of many particles.

We will, in this expansion theory, introduce the Hamilton-Cayley's theorem as our basic starting point, and extend it to a point appropriate for our expansion theory. Our theory may be called the expansion theory in terms of the matrix-traces of the first, second, third orders, and so on.

(5) The presentation of the second order approximation of the quantum radial distribution function by the W.K.B. approach within the framework of the Broyles program.

The theoretical result of this approximation is applicable universally for any kind of quantum fluid with one component in its equilibrium state. Two results applicable for the quantum fluids at high and fairly low temperatures will be presented by taking into account the quasi-quantum effect as well as the exchange effect of the quantum particles of the fluid under consideration. It would, in this presentation, be interesting to the reader that some hypersurface integrals related to this problem vanish for the volume of the quantum fluid large enough and in equilibrium. The new hypervolume integrals appearing in the course of the treatment of this problem are probably useful also for the treatment of other statistical-mechanical problems, and are presented in Appendices with their evaluated steps.

(6) The presentation of the comparison of the theoretical result with the experimental result of the quantum radial distribution function of the neon fluid to testify to the order of the accuracy of our approximation theory.

We will, in this presentation, be concerned with testing the order of the correctness of our approximation theory by comparing it with the radial distribution function determined experimentally by the measurement of the scattering intensity of x-rays by the neon liquid. This comparison will give us some aid for our further better idea leading to a better solution to this problem.

Finally, we will set up some notes about the notations to be used in the development of our theory immediately subsequent to this chapter. We are, in this dissertation, concerned with the quantum mechanical system of N(large enough) identical, indistinguishable, interacting particles. We will use the notation- and summation-conventions of tensor analysis in this discussion.

We assume the Euclidean character of the 3-dimensional realistic space* with the line element measured by the unit"cm," where each particle of the system occupies a point. We regard the realistic space as the covariant vector space of the position vector of a particle. Furthermore, we introduce the 3-dimensional abstract vector space reciprocal to the realistic space and also with the Euclidean character. Then, the line element of this reciprocal vector space is measured with the reciprocal unit "cm^{-1}," and therefore, this abstract reciprocal space can be regarded as the wave (or propagation) vector space of the particle.

---

*In the strict sense, this assumption is not correct from the standpoint of the theory of general relativity, even though we will introduce the interaction potential of N particles, in addition to this Euclidean character, corresponding to the fundamental metric tensor (not equal to Kronecker's δ) in the theory of general relativity.

Since the Euclidean character has been assumed for the realistic space, the contravariant vector space of the position vector of the particle is identical to its covariant vector space, i.e. the realistic space. Similarly, this is also the case for the reciprocal space. Thus, we see that the four kinds of spaces are mathematically identical to each other with no distinction between the covariant and contravariant components of a vector and two kinds of different units (cm and cm^{-1}) used for measurements of their line elements. Hence every mathematical operation can be defined numerically even between the vectors of the realistic and reciprocal spaces. For example, the scalar product $k_1 \cdot r_1$ between two vectors of the reciprocal and realistic spaces can be well defined even in the mathematically strict sense.

Since we have no distinction between the covariant-component indices(subscript) and the contravariant-component indices(superscript), we may represent the components $(x_\lambda^1, x_\lambda^2, x_\lambda^3)$ and $(k_\lambda^1, k_\lambda^2, k_\lambda^3)$ of the position and wave vectors $\vec{r}_\lambda$ and $\vec{k}_\lambda$ of the λth particle among the ordered N particles by

$$\vec{r}_\lambda \equiv (x_\lambda^i), \quad \vec{k}_\lambda \equiv (k_\lambda^i), \qquad (i=1,2,3) \quad . \tag{1}$$

We will use hereafter the Greek letters for the ordering subscripts of N particles, and the English letters for the ordering superscripts of the components of the vector quantities associated with each particle.

The important quantity q with which we will be confronted in the development of our main theory is, among all, the quantity of the following type of 3-dimensional scalar-product summation over all N particles of the system under consideration:

$$q = \vec{A}_\lambda \cdot \vec{B}_\lambda = A_\lambda^i B_\lambda^i \tag{2}$$

constructed by two vectors taken from one among the reciprocal and realistic spaces, or both. Eq. [2] can be rewritten in the form given by

$$q = A^{i}_{\lambda}\delta_{ij}\delta^{\lambda\mu}B^{j}_{\mu}, \qquad [3]$$

where δ_{ij} and $\delta^{\lambda\mu}$ are the subscripts and superscript Kronecker's δ, and we will use also the mixed-index Kronecker's δ, i.e., $\delta_{i}^{\ j}$, or $\delta_{\lambda}^{\ \mu}$, and we note, in Eq. [3], that the index λ, or μ runs from 1 to N, while the index i, or j, from 1 to 3.

Now, let us introduce the 3N-dimensional Euclidean configuration-space (mathematically identical to its reciprocal space) of the system under consideration, and $\vec{e}^{\,\lambda}_{i}$ (i=1,2,3;λ=1,2,...,N) be the fundamental unit vectors (3N in numer) of a 3N-dimensional orthogonal coordinate system established in the configuration space. We have, then,

$$\vec{e}^{\,\lambda}_{i}\cdot\vec{e}^{\,\mu}_{j} = \delta_{ij}\delta^{\lambda\mu}, \qquad [4]$$

and Eq. [3] is, by using Eq. [4], written in the following alternative form:

$$q = (A^{i}_{\lambda}\vec{e}^{\,\lambda}_{i})\cdot(B^{j}_{\mu}\vec{e}^{\,\mu}_{j}), \quad \text{or} \quad q = \vec{A}\cdot\vec{B}, \qquad [5]$$

by defining the two vectors $\vec{A}$ and $\vec{B}$ of the configuration (or reciprocal) space given by

$$\vec{A} \overset{\text{def.}}{\equiv} A^{i}_{\lambda}\vec{e}^{\,\lambda}_{i} \equiv (\vec{A}_1,\vec{A}_2,\ldots,\vec{A}_N); \quad \vec{B} \overset{\text{def.}}{\equiv} B^{j}_{\mu}\vec{e}^{\,\mu}_{j} \equiv (\vec{B}_1,\vec{B}_2,\ldots,\vec{B}_N) \qquad [6]$$

Eq. [5] shows us that the 3-dimensional scalar-product summation of Eq. [2] can be interpreted simply as the scalar product of the two vectors $\vec{A}$ and $\vec{B}$ defined by Eq. [6] in the 3N-dimensional configuration (or reciprocal) space of the system under consideration. Therefore, we

can, in our theory, recognize that N vector-quantities $\vec{A}_\lambda(\lambda=1,2,\ldots,N)$ associated with the same kind of quantities of N particles in the realistic (or reciprocal) space form together a vector $\vec{A}$ defined by Eq. [6] in the 3N-dimensional configuration (or reciprocal) space of the system under consideration. For example, we can regard the 3-dimensional scalar-product summation of the position vector $\vec{r}_\lambda$ and wave vector $\vec{k}_\lambda$ of each particle over all N particles of the system, i.e. $\vec{k}_\lambda \cdot \vec{r}_\lambda$ simply as the following dimensionless scalar product:

$$\vec{k}_\lambda \cdot \vec{r}_\lambda \equiv \vec{k} \cdot \vec{r} \qquad [7]$$

of two 3N-dimensional vectors $\vec{k}$ and $\vec{r}$ defined by

$$\begin{aligned} \vec{k} &\overset{\text{def.}}{=\!=} (\vec{k}_1, \vec{k}_2, \ldots, \vec{k}_N), \\ \vec{r} &\overset{\text{def.}}{=\!=} (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N), \end{aligned} \qquad [8]$$

and also

$$\vec{r}^2 \equiv \vec{r} \cdot \vec{r} = (x_\lambda^i \vec{e}_i) \cdot (x_\mu^j \vec{e}_j) = x_\lambda^i (\vec{e}_i \cdot \vec{e}_j) x_\mu^j$$

$$= x_\lambda^i \delta_{ij} \delta^{\lambda\mu} x_\mu^j = x_\lambda^i x_\lambda^i = \vec{r}_\lambda \cdot \vec{r}_\lambda$$

by using Eq. [4], or

$$\vec{r}^2 = \vec{r}_\lambda \cdot \vec{r}_\lambda, \text{ similarly } \vec{k}^2 = \vec{k}_\lambda \cdot \vec{k}_\lambda. \qquad [9]$$

Therefore, the total kinetic energy T of the system is given simply by

$$T = \frac{\hbar^2}{2m} \vec{k}_\lambda \cdot \vec{k}_\lambda = \frac{\hbar^2}{2m} \vec{k}^2 \quad . \qquad [10]$$

Next, the operators playing basic roles, with which we will be confronted in our later theory, are the following types:

$$\vec{k}_\lambda \cdot \vec{\partial}_\lambda f, \quad \vec{\partial}_\lambda \cdot \vec{\partial}_\lambda f, \quad \vec{\partial}_\lambda f \cdot \vec{\partial}_\lambda g, \quad \vec{k}_\lambda \vec{k}_\mu : \vec{\partial}_\lambda \vec{\partial}_\mu f, \qquad [11]$$

where the double dots ":" represent the scalar product of the two dyadics associated with it, and f, or g is a scalar function of the position vector $\vec{r} = (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$, and

$$\vec{\partial}_\lambda \overset{\text{def}}{\equiv\equiv} \cdot \nabla_{r_\lambda} \overset{\text{def}}{\equiv\equiv} \cdot \vec{e}_i \vec{\partial} / \partial x_\lambda^i \qquad [12]$$

with the fundamental unit vectors $\vec{e}_i$ (i=1,2,3) of a rectangular coordinate system $(x_\lambda^1, x_\lambda^2, x_\lambda^3)$ set up in the realistic space.

We seen, then, that

$$\vec{k}_\lambda \cdot \vec{\partial}_\lambda = k_\lambda^i \partial / \partial x_\lambda^i = k_\lambda^i \delta_{ij} \delta^{\lambda\mu} \partial / \partial x_\mu^j$$

$$= (k_\lambda^i \vec{e}_i^\lambda) \cdot (\vec{e}_j^\mu \partial / \partial x_\mu^j)$$

by using Eq. [4], or

$$\vec{k}_\lambda \cdot \vec{\partial}_\lambda = \vec{k} \cdot \vec{\partial} \qquad [13]$$

by using the definitions of Eq. [8] and

$$\vec{\partial} \overset{\text{def}}{\equiv\equiv} \cdot \vec{e}_j^\mu \partial / \partial x_\mu^j \equiv (\vec{\partial}_1, \vec{\partial}_2, \ldots, \vec{\partial}_N) \quad . \qquad [14]$$

Thus, the first of Eq. [11] can be expressed simply in the following form:

$$\vec{k}_\lambda \cdot \vec{\partial}_\lambda f = \vec{k} \cdot \vec{\partial} f \qquad [15]$$

by using the 3N-dimensional gradient operator $\vec{\partial}$ defined by Eq. [14]. Similarly, the second of Eq. [11] is written simply as

$$\vec{\partial}_\lambda \cdot \vec{\partial}_\lambda f = \vec{\partial} \cdot \vec{\partial} f \equiv \vec{\partial}^2 f \qquad [16]$$

by using the 3N-dimensional Laplacian operator $\vec{\partial}^2$ defined by

$$\vec{\partial}^2 \overset{\text{def}}{\equiv\equiv} \cdot (\partial / \partial x_\lambda^i)(\partial / \partial x_\lambda^i) = \vec{\partial}_\lambda \cdot \vec{\partial}_\lambda \quad . \qquad [17]$$

The other two of Eq. [9] are written similarly as

$$\vec{\partial}_\lambda f \cdot \vec{\partial}_\lambda g = \vec{\partial} f \cdot \vec{\partial} g,$$
$$\vec{k}_\lambda \vec{k}_\mu : \vec{\partial}_\lambda \vec{\partial}_\mu f = \vec{k}\vec{k} : \vec{\partial}\vec{\partial} f \quad . \qquad [18]$$

The differential operator T of the total kinetic energy of the system under consideration is, in this fashion, expressed simply by

$$T = -\frac{\hbar^2}{2m} \vec{\partial}_\lambda \cdot \vec{\partial}_\lambda = -\frac{\hbar^2}{2m} \vec{\partial}^2 \qquad [19]$$

just as in the case of one particle.

We will, though not so frequently, be confronted with the need of the gradient operator in the reciprocal space. However, we designate this operator by the notation given by

$$\vec{a} \overset{\text{def}}{\equiv\equiv} \cdot e_i^\lambda \partial/\partial k_\lambda^i \equiv (\vec{a}_1, \vec{a}_2, \ldots, \vec{a}_N), \qquad [20]$$

and correspondingly, the 3N-dimensional Laplacian operator by

$$\vec{a}^2 \overset{\text{def}}{\equiv\equiv} \cdot (\partial/\partial k_\lambda^i)(\partial/\partial k_\lambda^i) = \vec{a}_\lambda \cdot \vec{a}_\lambda \quad . \qquad [21]$$

The introductions of those notations stated above are presented in the hope that the complicated many-body problem may be reduced, even notationally, to one particle problem by avoiding the tedious, misleading, various kinds of indices, multiple summation and product notations in the conventional notation-fashion, within which no mistakes arise. Under this idea, we will have below further introduction of still more notations.

The differential operators corresponding to the position and wave vector operators $(\vec{r}, \vec{k})$ of the system is given by

$$\vec{r} = i\hbar\vec{a}, \quad \vec{k} = -i\vec{\partial}. \qquad [22]$$

We will use the following hypervolume-element notations in the 3N-dimensional configuration and reciprocal spaces respectively:

$$d\tau \overset{\text{def.}}{=\!=} \prod_{\lambda=1}^{N} d^3\vec{r}_\lambda \overset{\text{def.}}{=\!=} d^{3N}\vec{r}, \quad d\tau' \overset{\text{def.}}{=\!=} \prod_{\mu=3}^{N} d^3\vec{r}_\mu \overset{\text{def.}}{=\!=} d^{3N-6}\vec{r} \ ,$$

$$d\omega \overset{\text{def.}}{=\!=} \prod_{\lambda=1}^{N} d^3\vec{k}_\lambda \overset{\text{def.}}{=\!=} d^{3N}\vec{k}, \qquad [23]$$

and the following integral-domain notations:

$$\tau \overset{\text{def.}}{=\!=} V^N, \quad \tau' \overset{\text{def.}}{=\!=} V^{N-2} \qquad [24]$$

for the integration with respect to the variables $(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ and $(\vec{r}_3, \vec{r}_4, \ldots, \vec{r}_N)$ over the volume V of the realistic space respectively. Corresponding to τ', we will frequently use also the notation written by

$$\vec{r}' \overset{\text{def.}}{=\!=} (\vec{r}_3, \vec{r}_4, \ldots, \vec{r}_N). \qquad [25]$$

The notations dS and ds will stand for the $\{3(N-2)-1\}$-dimensional hypersurface element in the $3(N-2)$-dimensional space and the surface element in the realistic space respectively, and the single integral notation will stand for any kind of multiple integral notation, i.e

$$\int \overset{\text{def.}}{=\!=} \iint \cdots \int \qquad [26]$$

and for any kind of hypersurface integral, i.e.

$$\oint \overset{\text{def.}}{=\!=} \oiint \cdots \oint \ . \qquad [27]$$

In this way, we can deal with the many body problem notationally just as the one particle problem by using the usual 3-dimensional analysis, as long as we are concerned with our theory to be presented in this dissertation.

We have, in quantum statistical mechanics, an important parameter β closely corresponding to the time parameter t in the Schrödinger-Heisenberg quantum mechanics. This parameter is defined by

$$\beta = 1/(kT) \qquad [28]$$

with the absolute temperature T of the system under consideration and the Boltzmann's constant k. We will use the following notations about the derivatives with respect to these two parameters t and β:

$$\partial_t \overset{\text{def}}{\equiv\equiv} \cdot\partial/\partial t, \quad \partial_\beta \overset{\text{def}}{\equiv\equiv} \cdot\partial/\partial\beta \quad . \qquad [29]$$

The configuration, or reciprocal space may be regarded as the dimension space, of which each point labels each coordinate axis of the $\vec{r}$-representation, or $\vec{k}$-representation in the Hilbert space. We represent the total number of dimensions of the Hilbert space of which each dimension (or coordinate axis) corresponds to a point of a curve, surface, and volume, notationally by

$$\infty^1, \infty^2, \infty^3 \quad .$$

Therefore, the total number of dimensions of the Hilbert space of which the dimension space is given by the configuration, or reciprocal space, is given notationally by

$$\infty^{3N}.$$

We represent the fundamental orthonormal bra-vectors of ∞^{3N} in number in the $\vec{r}$-representation, or the $\vec{k}$-representation of the Hilbert space by

$$\langle \vec{r}\,'s| \overset{\text{def}}{\equiv\equiv} \cdot\langle \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N| \equiv {}_1\langle \vec{r}_1|{}_2\langle \vec{r}_2| \cdots {}_N\langle \vec{r}_N|,$$

$$\langle \vec{k}\,'s| \overset{\text{def}}{\equiv\equiv} \cdot\langle \vec{k}_1, \vec{k}_2, \ldots, \vec{k}_N| \equiv {}_1\langle \vec{k}_1|{}_2\langle \vec{k}_2| \cdots {}_N\langle \vec{k}_N| \quad . \qquad [30]$$

We make a distinction between $\langle \vec{r}'s|$ and $\langle \vec{r}|$, similarly, $\langle \vec{k}'s|$ and $\langle \vec{k}|$. The meanings of the two bra vectors $\langle \vec{r}|$ and $\langle \vec{k}|$ will be manifested in the middle part of the next chapter.

Since the time variable t is regarded as a parameter in the Schrödinger-Heisenberg quantum mechanics as stated above, it is rather reasonable that we express the state function $\Psi(\vec{r},t)$ of the system under consideration by

$$\Psi(\vec{r},t) \equiv \langle \vec{r}|;t\rangle, \qquad [31]$$

instead of expressing it by

$$\Psi(\vec{r},t) \equiv \langle \vec{r},t|\Psi\rangle \ .$$

This latter notation is rather reasonable in the Dirac-Feymann relativistic (special, not general) quantum mechanics. Therefore, in our theory to be developed immediately from the next chapter, the ket-vector denoted by

$$|;t\rangle \qquad [32]$$

represents an arbitrary, normalized, state ket-vector, corresponding to the state function $\Psi(\vec{r},t)$ which is a component of the state ket-vector of Eq. [32] along a coordinate axis of the $\vec{r}$-representation labeled by $\vec{r} \equiv (\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ in the ∞^{3N}-dimensional Hilbert space (≡a linear manifold).

CHAPTER II

THE FUNDAMENTAL THEORY OF QUANTUM STATISTICAL MECHANICS

—Willst du immer weiter schweifen? Sieh! das Gute
liegt so nah. Lerne nur das Glück ergreifen,
Denn das Gluck ist immer da.—(Goethe)

2.1. The Introduction of the Statistical Density Operator

Let us consider a quantum-mechanical system composed of N particles (atoms, molecules, etc.) with a Hamiltonian operator H. The state ket-vector $|;t\rangle$ of the system develops, in S-picture, according to the time-dependent Schrödinger's equation given by

$$i\hbar\partial_t|;t\rangle = H|;t\rangle \quad , \tag{1}$$

or in its equivalent form:

$$|;t\rangle = e^{-iH(t-t_o)/\hbar}|;t_o\rangle \tag{2}$$

if the system is conservative.

The probability density $w(t;\vec{r},\vec{r})$ of finding the system in a unit volume about a point $\vec{r}$ at a time-point t in its 3N-dimensional configuration space is

$$w(t;\vec{r},\vec{r}) \overset{\text{def}}{=\!=} \cdot |\langle\vec{r}|;t\rangle|^2 = \langle\vec{r}|;t\rangle\langle;t|\vec{r}\rangle \tag{3}$$

according to M. Born's interpretation.[1] We regard the following mathematical object W(t) defined by

$$W(t) \overset{\text{def}}{=\!=} \cdot |;t\rangle\langle;t| \tag{4}$$

as an operator (or an observable) in functional space (or Hilbert's space) corresponding to the classical phase space.

The probability density $w(t;\vec{r},\vec{r})$ defined by Eq. (3) may, then, be written in the form:

$$w(t;\vec{r},\vec{r}) \equiv \langle\vec{r}|W(t)|\vec{r}\rangle \ , \tag{5}$$

which is the quantum-mechanical expectation value of the observable $W(t)$ at the state of the position eigenket $|\vec{r}\rangle$. Eq. (5) may be regarded also as a diagonal element of the representatives of the operator $W(t)$ in the representation of the position eigenkets, i.e., $|\vec{r}\rangle$ so that the nondiagonal element of this representatives is given by

$$w(t;\vec{r},\vec{r}') \equiv \langle\vec{r}|W(t)|\vec{r}'\rangle \ . \tag{6}$$

This representatives forms a continuous matrix which is called the quantum-mechanical probability density matrix of the system.

Now, let us consider the representatives of this operator $W(t)$ in a representation $|q\rangle$ defined by the eigenkets $|q\rangle$'s of an observable Q of the system, i.e.

$$Q|q\rangle = q|q\rangle \ . \tag{7}$$

It becomes, then,

$$w(t;q,q') = \langle q|W(t)|q'\rangle = \langle q|;t\rangle\langle;t|q'\rangle,$$

of which the diagonal element becomes

$$w(t;q,q) = |\langle q|;t\rangle|^2 \ . \tag{8}$$

This implies physically that the diagonal element of the representatives of the operator $W(t)$ in the representation of the observable Q represents the probability of obtaining the measurable value q of the observable if a measurement of it is done on the system at the state $|;t\rangle$. Eqs. (8) and (5) show us, therefore, that the information about the

probability of obtaining the measurable value of every observable of the system at the state $|;t\rangle$ is contained in the operator $W(t)$ defined by Eq. (4), which is intrinsic to the system under consideration. We call, therefore, the operator $W(t)$ the quantum-mechanical probability density operator, or briefly the Born's density operator of the system, since M. Born has given first the probability interpretation of Eq. (3) to the state function $\langle\vec{r}|;t\rangle$.

The combination of Eq. (4) with Eq. (2) gives the following alternative form of Born's density operator:

$$W(t) \equiv e^{-iH(t-t_o)/\hbar}|;t_o\rangle\langle;t_o|e^{iH(t-t_o)/\hbar} \quad ,$$

or

$$W(t) \equiv e^{-iHt/\hbar}|;0\rangle\langle;0|e^{iHt/\hbar} \quad , \tag{9}$$

if we take $t_o = 0$, which expresses the time-development of the Born's density operator of the system starting from the initial state $|;0\rangle$. It is easy, from Eq. (9), or Eq. (4), to see that

$$\frac{d}{dt}\langle;t|W(t)|;t\rangle = 0 \quad , \tag{10}$$

by noting

$$\langle;t|W(t)|;t\rangle = 1$$

coming from the normalized character of the state vector $|;t\rangle$. Eq. (10) may be reduced to its equivalent form:

$$i\hbar\partial_t W(t) + [W(t),H] = 0 \tag{11}$$

by using Eq. (1), or Eq. (2). It can be shown physically that Eq. (11) is the formal form of the law of conservation of the probability of finding the system at the state $|;t\rangle$ at a time-point t, or at a point $\vec{r}$

in its 3N-dimensional configuration space. The value of the invariant trace of Born's density operator under any similar transformation is unity, i.e.

$$\mathrm{Tr}(W(t)) = 1, \tag{12}$$

and Born's density operator $W_H(t)$ in H-picture is time-independent and given by the initial Born's density operator $W(0)$ in S-picture, i.e.

$$W_H(t) = W(0) = |;0\rangle\langle;0| \ .$$

The expectation value $\langle Q\rangle$ of an observable Q at the state $|;t\rangle$ is given by

$$\langle Q\rangle = \mathrm{Tr}(WQ) = \mathrm{Tr}(QW) \ . \tag{13}$$

Born's density operator $W(t)$ is an Hermitian projection-operator (an idempodent) to project any vector onto the state vector $|;t\rangle$ and has the state vector as its eigenket vector corresponding to the eigenvalue 1 among two possible eigenvalues 1 and 0. Besides those properties stated above, this operator has many interesting properties. A systematic and complete presentation of these properties of Born's density operator may be seen from several papers published recently by several authors.[2,3,4,5,6,7,8]

However, we are not, in this dissertation, concerned directly with the Born's density operator $W(t)$. We omit, therefore, our further discussions about it. We are going to introduce another density operator useful for quantum statistical mechanics starting with Born's density operator by taking another point of view different from those of recent authors.

We consider, at first, the behavior of the state vector $|;t\rangle$ in the functional space of dimension ∞^{3N}. Suppose the continuous set S

is composed of every ket vector normalizable to unity in this functional space. It is, then, evident that this continuous set S forms the hypersurface of $(\infty^{3N}-1)$-dimensional unit sphere in the ∞^{3N}-dimensional functional space and all accessible state vectors $|;t\rangle$ normalizable to unity form a subset s of the continuous set S, i.e

$$s \subset S \quad . \tag{14}$$

Thus, all accessible state vectors occupy a part of S since every element of the subset s must be expanded in the following limited form:

$$|;t\rangle = \sum_{\vec{n}} a_{\vec{n}} e^{-iE_{\vec{n}}t/\hbar} |\vec{n}\rangle \tag{15}$$

in addition to the normalization requirement. $a_{\vec{n}}$ is, in general, the complex constant coefficient independent of the time parameter t, and $|\vec{n}\rangle$ satisfies

$$H|\vec{n}\rangle = E_{\vec{n}}|\vec{n}\rangle \quad .^{1} \tag{16}$$

Furthermore, the state vector $|\beta';t\rangle$ [2] starting with an initial state $|\beta'\rangle$ moves in accordance with Eq. (2), i.e.

$$|\beta';t\rangle = e^{-iHt/\hbar}|\beta'\rangle \ , \tag{17}$$

and the terminus of $|\beta';t\rangle$ describes a state trajectory in the domain s on the hypersurface of the unit sphere described above. It can be, then, shown easily not only that every state vector corresponding to every time point, i.e. every point on a state trajectory cannot, in

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[1] $\vec{n}$ is a lattice vector in quantum number vector space, and we note here that the subset s is a closed linear manifold.

[2] β' is a labeling parameter which has very significant physical meaning as we will see later.

general, be orthogonal to each other but also that every state trajectory starting from different initial state never intersect with each other. This proposition may be proved by using the quantum-mechanical law of causality, i.e., the law of the unique determinancy of the state vector for a given initial state.[7] This property of non-intersection of every state trajectory is very important in formulating the basic principles of quantum statistical mechanics.

Now, we classify every accessible state trajectory into two categories according to whether the initial state $|\beta'\rangle$ is an energy eigenstate $|\vec{n}\rangle$ or not. Let us call the system starting initially from an energy eigenstate the first kind of system, and the system starting initially from non-energy eigenstate the second kind of system. This classification is reasonable since the state of the system at an arbitrary time point can be determined uniquely only by its initial state according to the quantum-mechanical law of causality. We may, thus, decompose the set $\{|\beta'\rangle\}$ of every accessible initial state into two subsets, i.e., $\{|\vec{n}\rangle\}$, the set of every eigenstate of energy, and $\{|\beta\rangle\}$, the set of every non-eigenstate of energy of the system, or

$$\{|\beta'\rangle\} = \{|\vec{n}\rangle\} + \{|\beta\rangle\} . \tag{18}$$

Correspondingly, the subset s is decomposed again into two subsets s_1 and s_2, or

$$s = s_1 + s_2, \tag{19}$$

where s_1 corresponds to the first kind of system, and s_2, the second kind of system.

Next, we will analyze the properties of each of the systems belonging to these two categories respectively.

A. The First Kind of System s_1:

Since the first kind of system is defined by

$$|\beta'\rangle = |\vec{n}\rangle,$$

the equation of time development of the state of this system becomes, in accordance with Eq. (17),

$$|\vec{n};t\rangle = e^{-itH/\hbar}|\vec{n}\rangle \ ,$$

or

$$|\vec{n};t\rangle = e^{-i\omega_{\vec{n}}t}|\vec{n}\rangle \tag{20}$$

by using Eq. (16) and putting

$$E_{\vec{n}} = \hbar\omega_{\vec{n}} \quad . \tag{21}$$

Eq. (20) refers to a stationary state of the system with a conservative energy eigenvalue $E_{\vec{n}}$ so that the terminus of the state vector given by Eq. (20) is moving along its state trajectory on the hyperspherical surface of unit sphere with an invariant energy $E_{\vec{n}}$.[3]

Our next question is whether this trajectory is closed or not. If we can find a time point t such that

$$|\vec{n};t\rangle = |\vec{n}\rangle, \quad \text{or} \quad e^{-i\omega_{\vec{n}}t}|\vec{n}\rangle = |\vec{n}\rangle. \tag{22}$$

We can, then, conclude that this trajectory is a closed curve on the hypersurface of unit sphere. Actually, this conclusion is correct. It is as follows: If we put, in Eq. (22),

$$t = 2\pi\ell/\omega_{\vec{n}}, \quad (\ell=0,\pm1,\pm2,\ldots),$$

Eq. (22) is, then, satisfied since this value of t makes the exponential

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[3]We note here that $|\vec{n}\rangle$ and $e^{-i\omega_{\vec{n}}t}|\vec{n}\rangle$ represent the same physical state, but they are different ket (or state) vectors from each other.

function of Eq. (22) be unity. This shows us that the state vector comes back to its initial state vector with a period τ given by

$$\tau = 2\pi/\omega_{\vec{n}} = h/E_{\vec{n}} \quad , \tag{23}$$

that is, the state vector is moving periodically along its trajectory with a definite angular frequency $\omega_{\vec{n}}$ given by

$$\omega_{\vec{n}} = E_{\vec{n}}/\hbar \quad .$$

This is a different point of view for $\omega_{\vec{n}}$ from those of de Broglie and Bohr.[4] We should note here that every trajectory of the stationary state vector labelled by a different lattice vector $\vec{n}$ of quantum numbers never, as we have seen already, intersects with each other in addition to its property of closeness. The number of trajectories of stationary state vectors is the same as the number of the lattice points $\vec{n}$'s in quantum number vector space, which is, in general, infinite.

Next, we will investigate Born's density operator $W_{\vec{n}}(t)$ for this system. The second term (commutator) of Eq. (11) is equal to

$$= e^{-iHt/\hbar}[W_{\vec{n}}(0),H]e^{iHt/\hbar}$$

$$= e^{-iHt/\hbar}(H|\vec{n}\rangle\langle\vec{n}| - |\vec{n}\rangle\langle\vec{n}|H)e^{iHt/\hbar} = 0$$

by using Eq. (16). We see, therefore, that

$$\partial_t W_{\vec{n}}(t) = 0,$$

i.e., time-dependent of Born's density operator for the first kind of system. Actually, we have, from Eq. (9),

$$W_{\vec{n}}(t) = |\vec{n}\rangle\langle\vec{n}| = W_{\vec{n}}(0). \tag{24}$$

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[4] For example, see A. Messiah; Quantum Mechanics, Vol. 1, Chapter 1 and 2, (1961).

We have, so far, assumed tacitly that the energy eigenvalue $E_{\vec{n}}$ of the system is not degenerate. In systems made up of very large numbers of molecules, the energy levels will, in general, be highly degenerate. Let

$$|\vec{n},j;t\rangle = e^{-iE_{\vec{n}}t}|\vec{n},j\rangle, \quad (j=1,2,\ldots,f) \tag{25}$$

be orthonormalized degenerate (f-fold) stationary states corresponding to an energy level $E_{\vec{n}}$. The Born's density operator $W_{\vec{n},j}(t)$ for the jth degenerate stationary vector $|\vec{n},j;t\rangle$ is, then, given by

$$W_{\vec{n},j}(t) = |\vec{n},j;t\rangle\langle\vec{n},j;t| \ .$$

There are f Born's density operators $W_{\vec{n},j}(t)$ (j=1,2,...,f) corresponding to this one energy level $E_{\vec{n}}$. All of these density operators of f in number are density operators of <u>pure states</u>. For the statistical information of the isolated system specified by the energy $E_{\vec{n}}$, it is plausible to take the time-average of those f Born's density operators $W_{\vec{n},j}(t)$ (j=1,2,...,f) under some statistical weight. As we will prove in Eq. (37)(take $|\beta\rangle = |\vec{n},j\rangle$ in Eq. (37)), this statistical weight is independent of the time variable t and the subscript j. Therefore, the time averaged Born's density operator $D_{\vec{n}}$ is given by

$$D_{\vec{n}} \overset{\text{def.}}{\equiv\equiv} \sum_{j=1}^{f} \oint_{c_j} dt W_{\vec{n},j}(t) \Big/ \sum_{j=1}^{f} \oint_{c_j} dt, \tag{26}$$

where c_j is the closed trajectory of the stationary state vector $|\vec{n},j;t\rangle$, and the contour integral goes along the closed trajectory curve c_j.

Equation (26) reduces to

$$D_{\vec{n}} = \sum_{j=1}^{f} \tau_j W_{\vec{n},j}(0) \Big/ \sum_{j=1}^{f} \tau_j, \tag{27}$$

with the period τ_j of the state vector $|\vec{n},j;t\rangle$. As we have shown

already in Eq. (23), the period τ_j depends upon only the energy level $E_{\vec{n}}$, but not upon its degenerate states, i.e. the subscript j. We have, therefore,

$$\tau_1 = \tau_2 = \cdots\cdots = \tau_f (\equiv h/E_{\vec{n}}) \ . \tag{28}$$

The combination of Eq. (28) with Eq. (27) gives

$$D_{\vec{n}} = \frac{1}{f} \sum_{j=1}^{f} W_{\vec{n},j}(0) = \frac{1}{f} \sum_{j=1}^{f} |\vec{n},j\rangle\langle\vec{n},j| \ . \tag{29}$$

This is the statistical density operator of <u>mixed states</u> useful for the statistical information of an isolated system with a specified energy level $E_{\vec{n}}$. We call this density operator <u>the Neumann's density operator of first kind</u>. The macroscopic quantity corresponding to an observable Q of the isolated system may be defined by the time-average of the expectation value $\langle Q \rangle$ of the observable Q, and shown easily to be

$$\overline{\langle Q \rangle} = \mathrm{Tr}(QD_{\vec{n}}) \ . \tag{29}'$$

The right-hand side of Eq. (29)' represents the microcanonical ensemble-average in the ensemble theory. Therefore, Eq. (29)' shows us the correctness of the quantum-mechanical ergodic hypothesis, i.e., the hypothesis that the time-average of an observable is equal to the ensemble average of the observable.

It is instructive to note here that we never have used the postulate of equal a priori probability in deriving the correct form of Eq. (29) of the Neumann's density operator of first kind, and instead, we have used the postulate of Eq. (37) that the statistical weight in the time-average of Born's density operator is inversely proportional

to the speed of the terminus of the state vector at a time point t on its trajectory [5].

Next, we are in the position to analize the properties of the second kind of system.

B. The Second Kind of System s_2:

Since the second kind of system is, as stated in Eq. (18), defined by

$$|\beta'\rangle = |\beta\rangle,$$

we have, from Eq. (17), the following equation of time development of the state of this system:

$$|\beta;t\rangle = e^{-iHt/\hbar}|\beta\rangle \tag{30}$$

with $|\beta\rangle$ not being an energy eigenket at the time t = 0. A further change in Eq. (30) may be made by inserting the identity operator given by

$$I \equiv \sum_{\vec{n}} |\vec{n}\rangle\langle\vec{n}| \quad [6] \tag{31}$$

between the exponential operator and the vector $|\beta\rangle$ in the right-hand side of Eq. (30). It is as follows:

$$|\beta;t\rangle = \sum_{\vec{n}} e^{-i\omega_{\vec{n}}t}|\vec{n}\rangle\langle\vec{n}|\beta\rangle \tag{32}$$

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[5] This postulate is more basic than other authors have recognized so far. For example, see T. L. Hill; Statistical Mechanics (1956), p 40 et seq.

[6] We assume here that the Hamiltonian operator H has no continuous eigenvalues. But our subsequent discussions can be extended easily even to the case of continuous eigenvalue of H.

by using Eqs. (21) and (16).

Our next problem is to see whether the state trajectory given by Eq. (32) on the hyperspherical surface in functional space is open, or closed. In other words, does there exist a time-point t such that

$$|\beta;t\rangle = |\beta\rangle \quad ? \tag{33}$$

The substitution of Eq. (32) into the left-hand side of Eq. (33) and the use of the identity operator given by Eq. (31) for the right-hand side of Eq. (33) lead to

$$\sum_{\vec{n}} |\vec{n}\rangle\langle\vec{n}|\beta\rangle(1-e^{-i\omega_{\vec{n}}t}) = 0.$$

We must, therefore for all $\vec{n}$, have

$$e^{-i\omega_{\vec{n}}t} = 1 , \tag{34}$$

since the $|\vec{n}\rangle$'s are linearly independent of each other and $\langle n|\beta\rangle \neq 0$ in accordance with no intersection (Durchschnitt) between two subsets s_1 and s_2 defined by Eq. (19). Eq. (34) requires that

$$\omega_{\vec{n}}t = 2\pi\ell_{\vec{n}}$$

with no dependence of t on $\vec{n}$, where $\ell_{\vec{n}}$ is an arbitrary integer which is possibly dependent on $\vec{n}$. This shows us that

$$E_{\vec{n}}/\ell_{\vec{n}} = h/t \text{ (independent of } \vec{n}),$$

or

$$E_{\vec{n}}:E_{\vec{n}'}:E_{\vec{n}''}:\ldots\ldots = \ell_{\vec{n}}:\ell_{\vec{n}'}:\ell_{\vec{n}''}:\ldots\ldots \quad .$$

The energy level $E_{\vec{n}}$ of the system under consideration must, therefore, be proportional to integer $\ell_{\vec{n}}$ in order that the state trajectory of Eq. (32) can be closed. This requirement is, in general, impossible

except in the case of non-interacting harmonic oscillator system. Therefore, the state trajectory of the second kind of system does not, in general, close as in the case of the first kind of system. The terminus of the state vector $|\beta;t\rangle$ describes an open curve in the domain s_2 on the hypersurface of the unit sphere in functional space. Our subsequent question is as follows: Is it a Peano curve, or an open Jordan curve?(9) It seems that this question is a difficult problem to be solved.[7] However, fortunately, we are not here concerned directly with this question in setting up our fundamental principles of quantum statistical mechanics.

Our next problem is to examine whether the Born's density operator of this kind of system is dependent on time, or not. The commutator in the second term of Eq. (11) is, by using Eqs. (32), (31), and (24),

$$= e^{-iHt/\hbar} \sum_{\vec{n}} E_{\vec{n}} [\, |\beta\rangle\langle\beta|, W_{\vec{n}}] \, e^{iHt/\hbar} \neq 0 \ .$$

Therefore, the Born's density operator $W(t)$ for this system depends upon time, i.e. $W(t)$ is changing as the state vector $|\beta;t\rangle$ moves along its trajectory. Actually, this operator is, by using Eq. (32), expressed explicitly as follows:

$$W(t) = \sum_{\vec{n}} |\vec{n}\rangle \, |\langle\vec{n}|\beta\rangle|^2 \langle\vec{n}|$$

$$+ \sum_{\substack{\vec{n},\vec{n}' \\ (\vec{n}\neq\vec{n}')}} e^{-i(\omega_{\vec{n}}-\omega_{\vec{n}'})t} |\vec{n}\rangle\langle\vec{n}|\beta\rangle\langle\beta|\vec{n}'\rangle\langle\vec{n}'| \ , \qquad (35)$$

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[7] We note that Peano curve corresponds to Baltzmann's ergodic hypothesis and Jordan curve corresponds to Neumann-Birkoff's quasi-ergodic hypothesis.

where we used the definition given by Eq. (21). It should, in Eq. (35), be noted that the first summation term is time-independent while the second double-summation term is time-dependent but sinusoidally oscillatory.

Now, we are going to prove the validity of the postulate of a priori probability for this system. We are, at first, interested in seeing how much time is needed in changing the state vector $|\beta;t\rangle$ by a given infinitesimal norm of its displacement $\| d|\beta;t\rangle \|$ during its course of motion, and how the corresponding infinitesimal time dt depends upon the position of $|\beta;t\rangle$ on its trajectory.[8] We start with the differential form of the following Schrödinger's time-dependent equation:

$$i\hbar d|\beta;t\rangle = dtH|\beta;t\rangle \ , \text{ or } -i\hbar\langle\beta;t|d = \langle\beta;t|Hdt.$$

The Hermitian scalar product of these two equations gives

$$\langle\beta;t|H^2|\beta;t\rangle dt^2 = \hbar^2\|d|\beta;t\rangle\|^2 \qquad (36)$$

But, we have, by using Eq. (30) in the left-hand side of Eq. (36),

$$\langle\beta:t|H^2|\beta;t\rangle = \langle\beta|H^2|\beta\rangle \ ,$$

and we express the given infinitesimal norm by

$$ds \overset{\text{def}}{=\!=} \|d|\beta;t\rangle\| \ .$$

We have, then from Eq. (36),

$$dt = \hbar ds/(\langle\beta|H^2|\beta\rangle)^{\frac{1}{2}} \ , \qquad (37)$$

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[8] $\| d|\beta;t\rangle\| \overset{\text{def}}{=\!=}$ (the norm of $d|\beta;t\rangle$) $= [(d|\beta;t\rangle)^{\dagger}(d|\beta;t\rangle)]^{\frac{1}{2}}$; $\dagger$ = (Hermitian conjugate).

which is not dependent upon the point, i.e. the time-point on the trajectory in the course of motion of the state vector. In other words, the infinitesimal time dt during which the state vector stays at every point on its trajectory is the same. This implies physically that the probability of finding the system at every point on its trajectory is the same, i.e. the validity of the postulate of a priori probability for the quantum-mechanical state.

Equation (37) is written also as

$$\frac{ds}{dt} = \left\{ \sum_{\vec{n}} \omega_{\vec{n}}^2 | \langle \vec{n} | \beta \rangle |^2 \right\}^{\frac{1}{2}} \tag{38}$$

by having a change given by:

$$\langle \beta | H^2 | \beta \rangle = \sum_{\vec{n}} \langle \beta | H | \vec{n} \rangle \langle \vec{n} | H | \beta \rangle$$

$$= \hbar^2 \sum_{\vec{n}} \omega_{\vec{n}}^2 | \langle \vec{n} | \beta \rangle |^2 \quad .$$

Equation (38) may be interpreted physically as the speed of the terminus of the state vector $|\beta;t\rangle$ on its trajectory, which does not depend upon time but does depend on its initial state vector $|\beta\rangle$. That is, the representative point of state of the system has an open hypercurvilinear motion with an uniform speed on the hypersurface of unit sphere in Hilbert space. This situation is very much analogous to the realistic motion of uniform speed of a force-free particle constrained on a surface in realistic space, which moves, in general, along an open geodesic line on the constraining surface.(10) The same can be seen also from an Einstein's postulate of the theory of general relativity that a realistic mass point moves, without any 4-acceleration, along an open

geodesic line in 4-dimensional Riemanian time-space. Now, we are in a position to introduce Neumann's statistical density operator D_β by using our preliminary knowledge discussed so far.

Let us rewrite here Eq. (35) in the following form:

$$W(t) = \sum_{\vec{n},\vec{n}'} e^{-i(\omega_{\vec{n}}-\omega_{\vec{n}'})t} |\vec{n}\rangle\langle\vec{n}|\beta\rangle\langle\beta|\vec{n}'\rangle\langle\vec{n}'| \ . \tag{39}$$

As stated already, this Born's density operator of the second kind of system is varying with the position of the terminus of the state vector $|\beta;t\rangle$ on its trajectory, and the validity of the postulate of a priori probability, i.e. the possibility of the state vector staying equally at every time-point on its trajectory, has been proved. It is preferable to take the time-average of Born's density operator $W(t)$ given by Eq. (39) over the whole time-interval from the infinite past $t = -\infty$ to the infinite future $t = \infty$ for the statistical information of the system under consideration. It is, then, sufficient to take the time-average of $W(t)$ in usual sense in accordance with the proof or validity of the postulate of a priori probability. We have, therefore,

$$D_\beta \overset{\text{def.}}{\equiv} \overline{W(t)} = \sum_{\vec{n},\vec{n}'} |\vec{n}\rangle\langle\vec{n}|\beta\rangle\langle\beta|\vec{n}'\rangle\langle\vec{n}'|$$

$$\cdot \lim_{\tau\to\infty} \frac{1}{2\tau}\int_{-\tau}^{\tau} e^{-i(\omega_{\vec{n}}-\omega_{\vec{n}'})t}\, dt, \tag{AI}$$

or

$$D_\beta \equiv \sum_{\vec{n}} |\vec{n}\rangle |\langle\vec{n}|\beta\rangle|^2 \langle\vec{n}| \ , \tag{40}$$

by noting

$$\lim_{\tau\to\infty} \frac{1}{2\tau} \int_{-\tau}^{\tau} e^{-i(\omega_{\vec{n}}-\omega_{\vec{n}'})t}\, dt = \delta(\vec{n},\vec{n}') \quad .^{9} \qquad (40)'$$

This operator D_β is the time-averaged Born's density operator over whole trajectory of the state vector started initially from an accessible state specified by a parameter β. We will call this operator D_β the Neumann's statistical probability density operator, or briefly the Neumann's density operator of the system under consideration, since J. von Neumann has introduced firstly this operator according to his intuitive foresight without the basic discussions which are presented here in this paper.[11,12] The advantage of the Neumann's density operator D_β is especially in its universal character of use at every time-point irrespective of the time-point coordinate. Furthermore, this operator D_β is invariant in the sense that the initial state vector $|\beta\rangle$ can be replaced by any state vector $|\beta;t_o\rangle$ (t_o is arbitrary) corresponding to a point on the trajectory. For we have, by using Eqs. (30) and (16),

$$\begin{aligned}
&\sum_{\vec{n}} |\vec{n}\rangle |\langle\vec{n}|\beta\rangle|^2 \langle\vec{n}| \equiv D_\beta \\
&= \sum_{\vec{n}} |\vec{n}\rangle\langle\vec{n}|\beta\rangle\langle\beta|\vec{n}\rangle\langle\vec{n}| \\
&= \sum_{\vec{n}} |\vec{n}\rangle\langle\vec{n}| e^{iHt_o/\hbar} |\beta;t_o\rangle\langle\beta;t_o| e^{-iHt/\hbar} |\vec{n}\rangle\langle\vec{n}| \\
&= \sum_{\vec{n}} e^{i\omega_{\vec{n}} t_o} |\vec{n}\rangle\langle\vec{n}|\beta;t_o\rangle\langle\beta;t_o|\vec{n}\rangle\langle\vec{n}| e^{-i\omega_{\vec{n}} t_o} \quad ,
\end{aligned}$$

---

[9] Note that this integral represents also the curvilinear integral along the trajectory of state vector.

or

$$\sum_{\vec{n}} |\vec{n}\rangle |\langle \vec{n}|\beta\rangle|^2 \langle \vec{n}| = D_\beta = \sum_{\vec{n}} |\vec{n}\rangle |\langle \vec{n}|\beta;\tau_o\rangle|^2 \langle \vec{n}| \quad . \tag{41}$$

This invariant character of D_β assures us that we can write the initial state with $|\beta\rangle$ instead of writing with $|\beta;0\rangle$, so that β can be regarded as the labeling parameter of the trajectory instead of the labeling parameter of initial state vector, and also the ket vector $|\beta\rangle$ can be interpreted as the statistical state vector intrinsic to the trajectory specified by the labeling number β.

Now, we are going to modify our point of view for the trajectory of the state vector regarded as an orbit (or locus) of a moving point. Let us pick out a trajectory specified by a labeling number β, and look at all points on it statically. . Every point of it determines uniquely a state vector in Hilbert space respectively. We may, then, make a system correspond to each of the states so obtained as above. Thus, we obtain collection, or an ensemble of systems corresponding to the trajectory specified by β. Mathematically, this ensemble of systems is equivalent to the set of all points on the trajectory. Therefore, this ensemble of systems must be a continuous set specified by a labeling number β. Every system contained in this ensemble has to have the same Hamiltonian H, since the trajectory is intrinsic to not only the parameter β but also the Hamiltonian operator of the system under consideration. We must, therefore, use the Hamiltonian operator H and the parameter β in specifying the trajectory, or the ensemble of systems. Thus, we can consider that the abstract conception of state trajectory on the hypersurface of the unit hypersphere in Hilbert space

is nothing but an ensemble of realistic systems with a common Hamiltonian operator H and a common parameter β. Let us express this ensemble of realistic systems by the following symbol:

$$s_2(\beta,N,V;H)$$

where s_2 comes from Eq. (19), and N is the common total number of particles contained in the common volume V, of which the property of "commonness" has been assumed tacitly in our discussion done so far.

According to this point of view, the Neumann's density operator D_β defined by Eq. (40) can be interpreted as the ensemble-average of Born's density operator $W(t)$ over all elements of the continuous set $s_2(\beta,N,V;H)$ with continuous elements. It is instructive to note here that the time-average of the Born's density operator of the pure state is changed into the Neumann's density operator of the mixed state. In this sense, the Neumann's density operator can be used for the quantum statistical-mechanical information of the realistic equilibrium-system under consideration. The real number $|\langle\vec{n}|\beta\rangle|^2$ not greater than 1 in the Neumann's density operator D_β of Eq. (40) represents the statistical weight of mixing the density operators $|\vec{n}\rangle\langle\vec{n}|$'s of the pure states $|\vec{n}\rangle$'s. Quantum-mechanically, this weight of $|\langle\vec{n}|\beta\rangle|^2$ expresses the probability of finding the energy value $E_{\vec{n}}$ by the measurement of energy of the system when the system is at the state $|\beta\rangle$ right before the measurement done.

Finally, it should be mentioned that the Neumann's density operator of Eq. (40) can be used for the statistical description of an isothermal equilibrium system irrespective of the magnitude of the

particle number N and the volume V of the system. We will, hereafter, treat exclusively the quantum mechanical system in thermal equilibrium. Especially, in the theory of the quantum correlation function, we will assume also $H_i \langle\langle H$, where H_i is the interaction with a isothermal bath.

2.2 The General Properties of Neumann's Density Operator and the Determination of its Concrete Form

Before we determine the concrete form of Neumann's density operator, we will study the general properties of it preliminary to its determination. We will choose brief descriptions of proofs below.

Theorem 2.1:

$$D_\beta^\ell = \sum_{\vec{n}} |\vec{n}\rangle |\langle\vec{n}|\beta\rangle|^{2\ell} \langle\vec{n}| \quad , \quad (\ell=0,1,2,3,\ldots). \tag{42}$$

Proof: From Eq. (40), we have

$$D_\beta^2 = \sum_{\vec{n},\vec{n}'} |\vec{n}\rangle |\langle\vec{n}|\beta\rangle|^2 \langle\vec{n}|\vec{n}'\rangle |\langle\vec{n}'|\beta\rangle|^2 \langle\vec{n}'|$$

$$= \sum_{\vec{n}} |\vec{n}\rangle |\langle\vec{n}|\beta\rangle|^4 \langle\vec{n}|$$

by using the orthonormality of the complete set of eigenkets $|\vec{n}\rangle$'s. This procedure is continued to obtain the general form given by Eq. (42).

Theorem 2.2:

$$1 = \sum_{\vec{q}} \langle\vec{q}|D_\beta|\vec{q}\rangle^{10} = \mathrm{Tr}(D_\beta)$$

$$= \int_\infty d^{3N}\vec{r} \langle\vec{r}|D_\beta|\vec{r}\rangle = \int_\infty d^{3N}\vec{k} \langle\vec{k}|D_\beta|\vec{k}\rangle \quad . \tag{43}$$

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[10] The ket vector $|\vec{q}\rangle$ is the same vector as Eq. (7).

Proof:

$$\int_{\infty} d^{3N}\vec{r}\langle\vec{r}|D_\beta|\vec{r}\rangle = \sum_{\vec{n}} |\langle\vec{n}\,\beta\rangle|^2\langle\vec{n}|\left\{\int_{\infty} d^{3N}\vec{r}|\vec{r}\rangle\langle\vec{r}|\right\}|\vec{n}\rangle$$

$$= \sum_{\vec{n}} |\langle\vec{n}|\beta\rangle|^2\langle\vec{n}|\vec{n}\rangle$$

$$= \langle\beta|\left(\sum_{\vec{n}} |\vec{n}\rangle\langle\vec{n}|\right)|\beta\rangle$$

$$= \langle\beta|\beta\rangle = 1 \quad .$$

The others come immediately from the general character of invariance of trace of any operator in any representation.

Theorem 2.3: D_β is Hermitian and commutable with the Hamiltonian operator H, i.e.

$$D_\beta^\dagger = D_\beta, \quad [D_\beta, H] = 0, \tag{44}$$

i.e. D_β is an invariant operator (a constant of motion).

Proof:

$$[D_\beta, H] = \sum_{\vec{n}} |\langle\vec{n}|\beta\rangle|^2(H|\vec{n}\rangle\langle\vec{n}| - |\vec{n}\rangle\langle\vec{n}|H)$$

$$= \sum_{\vec{n}} |\langle\vec{n}|\beta\rangle|^2 E_{\vec{n}}(|\vec{n}\rangle\langle\vec{n}| - \vec{n}\rangle\langle\vec{n}|) = 0,$$

and the Hermitian property can be seen immediately from Eq. (40).

Theorem 2.4: The eigenvalue $P_{\vec{n}}(\beta)$ and eigenkets of D_β are given by

$$D_\beta|\vec{n}\rangle = P_{\vec{n}}(\beta)|\vec{n}\rangle \ , \tag{45}$$

$$P_{\vec{n}}(\beta) \overset{\text{def}}{=\!=} |\langle\vec{n}|\beta\rangle|^2 \quad .$$

Proof: From Eq. (40), we have

$$D_\beta = \sum_{\vec{n}'} |\vec{n}'\rangle|\langle\vec{n}'|\beta\rangle|^2\langle\vec{n}'| \quad .$$

Hence,
$$D_\beta|\vec{n}\rangle = \sum_{\vec{n}'} |\vec{n}'\rangle|\langle\vec{n}'|\beta\rangle|^2\langle\vec{n}'|\vec{n}\rangle$$
$$= |\langle\vec{n}|\beta\rangle|^2|\vec{n}\rangle \quad ,$$

which shows us that $P_{\vec{n}}(\beta) \equiv |\langle\vec{n}|\beta\rangle|^2$ is the eigenvalue of D_β corresponding to the eigenket $|\vec{n}\rangle$. This is trivial since two operators H and D_β are compatible with each other in accordance with Eq. (44).

Theorem 2.5: The time-average $\overline{\langle Q\rangle}$ of the expectation value $\langle Q\rangle$ of a time-independent observable Q at a state $|;t\rangle$ is, in terms of D_β, given by

$$\overline{\langle Q\rangle} = \mathrm{Tr}(QD_\beta) \quad . \tag{46}$$

Proof: See Appendix I. This theorem guarantees our foregoing statement that all statistical information of a system under consideration is contained in the Neumann's density operator D_β of the system. Equation (46) is comparable with Eq. (13), i.e. the quantum-mechanical average.

Now, we are going to determine uniquely the concrete form of Neumann's density operator by referring to the knowledge about D_β obtained above.

Theorems 2.2 and 2.5 shows us that the operator D_β may be regarded as an observable (with no classical analogy) concerned with the quantum-statistical probability density which corresponds to the classical distribution function. Furthermore, Theorem 2.4 shows us that the operator D_β is the observable giving the probability of obtaining the measurable value $E_{\vec{n}}$ of the energy observable H at the

statistical state $|\beta\rangle$. Theorem 2.3 shows us that the operator D_β takes the following form:

$$D_\beta = F(\beta, H) \tag{47}$$

since D_β must be an operator function of invariant operators, e.g. the Hamiltonian operator. This statement will be rather guaranteed by our subsequent discussions on the basis of the so-called "the law of large numbers."[11]

This law for canonical ensemble is, in terms of the terminology of this dissertation, given by

$$|\langle \vec{n}|\beta\rangle|^2 = e^{-E_{\vec{n}}/kT} \Big/ \sum_{\vec{n}} e^{-E_{\vec{n}}/kT} \quad (13) \tag{48}$$

Let us look carefully at the connection between both sides in Eq. (48). The independence of two ket vectors $|\vec{n}\rangle$ and $|\beta\rangle$ upon each other corresponds to that of the microscopic energy level $E_{\vec{n}}$ and the macroscopic absolute temperature T multiplied by the Boltzmann's constant k. Furthermore, we have only two kinds of parameters, i.e. $(\vec{n},\beta)$ in the left-hand side, $(\vec{n},T)$ or $(\vec{n},1/kT)$ in the right-hand side. We may, therefore, take the parameter β as

$$\beta = 1/kT \quad . \tag{49}$$

The parameter β introduced originally as a labeling index of the intial state (or statistical state) of the system under consideration is now interpreted as a macroscopic physical-quantity 1/kT, i.e. the reciprocal

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[11] See P 210 of the English translation edition of J. von Neumann; Mathematical Foundations of Quantum Mechanics translated by R. T. Beyer, Princeton University Press (1955).

of approximate thermal kinetic energy of a particle. This interpretation is also consistent with the hypothesis established in the end of the previous section since 1/kT has a continuous interval $(0,\infty)$.

We rewrite Eq. (48) in the form:

$$|\langle\vec{n}|\beta\rangle|^2 = e^{-\beta E_{\vec{n}}}/Q_\beta, \quad Q_\beta \overset{\text{def}}{=\!=} \sum_{\vec{n}} e^{-\beta E_{\vec{n}}} , \tag{50}$$

and combine this with Eq. (40), to see that

$$D_\beta = Q_\beta^{-1} \sum_{\vec{n}} e^{-\beta E_{\vec{n}}} |\vec{n}\rangle\langle\vec{n}| = Q_\beta^{-1} \sum_{\vec{n}} e^{-\beta H} |\vec{n}\rangle\langle\vec{n}|$$

$$= Q_\beta^{-1} e^{-\beta H} \Big(\sum_{\vec{n}} |\vec{n}\rangle\langle\vec{n}|\Big) ,$$

or

$$D_\beta = e^{-\beta H}/Q_\beta , \tag{51}$$

which is the form consistent with the required form given by Eq. (47). Equation (51) is the concrete form of Neumann's density operator which contains every statistical information concerned with canonical ensemble.

The macroscopic function Q_β of thermodynamical variables is, by using Eq. (43), determined as

$$Q_\beta = \mathrm{Tr}(D_\beta) \equiv \mathrm{Tr}(e^{-\beta H}) . \tag{52}$$

In the Hamiltonian representation, this invariant trace takes the form given by the second of Eq. (50). It has turned out easily that this function Q_β represents actually the partition function of the system in thermodynamical equilibrium.

Let us insert the identity operator:

$$I = \sum_{q} |q\rangle\langle q|$$

constructed from the discrete complete set $\{|q\rangle\}$ of the eigenket vectors of an arbitrary operator Q between the operator $e^{-\beta H}$ and the position eigenket vector $|\vec{r}\rangle$ in the following expression:

$$Q_\beta = \mathrm{Tr}\langle e^{-\beta H}\rangle = \int_{\infty} d^{3N}\vec{r}\langle\vec{r}|e^{-\beta H}|\vec{r}\rangle. \tag{53}$$

We obtain, then,

$$Q_\beta = \int_{\infty} d^{3N}\vec{r}\sum_{q}\langle q|\vec{r}\rangle e^{-\beta H}\langle\vec{r}|q\rangle \tag{54}$$

by changing the operator H into its equivalent differential operator. The function $S_\beta(\vec{r},\vec{r})$ defined by

$$S_\beta(\vec{r},\vec{r}) \overset{\mathrm{def}}{\equiv} N!\sum_{q}\langle q|\vec{r}\rangle e^{-\beta H}\langle\vec{r}|q\rangle = N!\langle\vec{r}|e^{-\beta H}|\vec{r}\rangle \tag{55}$$

is the so-called Slater sum in the discrete representation $|q\rangle$, which has been introduced firstly by J. C. Slater in 1931.[14] The partition function given by Eq. (54) is, then in terms of the Slater sum, written as

$$Q_\beta = \frac{1}{N!}\int_{\infty} d^{3N}\vec{r}S_\beta(\vec{r},\vec{r}). \tag{56}$$

Let us, next, consider the representatives of Neumann's density operator, especially in the $\vec{r}$- and $\vec{k}$-representations, respectively. We have, then,

$$D_\beta(\vec{r},\vec{r}') \overset{\text{def}}{\equiv} \cdot \langle \vec{r}| D_\beta |\vec{r}' \rangle = Q_\beta^{-1} \langle \vec{r}| e^{-\beta H(\vec{r},\vec{p})} |\vec{r}' \rangle$$

$$= Q_\beta^{-1} e^{-\beta H(\vec{r},-i\hbar\vec{\partial})} \langle \vec{r}|\vec{r}' \rangle \ ,$$

or

$$D_\beta(\vec{r},\vec{r}') = Q_\beta^{-1} e^{-\beta H(\vec{r},-i\hbar\vec{\partial})} \delta(\vec{r},\vec{r}'), \quad [12] \tag{57}$$

and we have, similarly,

$$D_\beta(\vec{k},\vec{k}') = Q_\beta^{-1} e^{-\beta H(i\hbar\vec{\partial},\hbar\vec{k})} \delta(\vec{k},\vec{k}') \ . \tag{58}$$

Next we are going to construct the so-called bridge differential equation between thermodynamics and quantum statistical mechanics by using Neumann's density operator D_β as a bridge connecting them and the well-known bridge algebraic equation:

$$Q_\beta = e^{-\beta F_\beta}, \quad \text{or} \quad \beta F_\beta = -\ell n Q_\beta \ , \tag{59}$$

where F_β is the Helmholtz free energy of the system in question. The differentiation of both sides of Eq. (51) with respect to β gives

$$(\partial_\beta \ell n Q_\beta) D_\beta + \partial_\beta D_\beta = -H D_\beta \ ,$$

which is combined again with Eq. (59), to give

$$(\partial_\beta + H) D_\beta = (F_\beta + \beta \partial_\beta F_\beta) D_\beta \ . \tag{60}$$

This differential equation of operator is the so-called bridge differential equation connecting between the microscopic world and macroscopic

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[12] $\delta(\vec{r},\vec{r}') \overset{\text{def}}{\equiv} \cdot \langle \vec{r}|\vec{r}' \rangle$, which is not the product of Dirac's δ-function in the usual sense. See Section 2.3, Eq. (90).

world. Equation (59) is derivable from Eq. (60) by using the temperature-boundary condition:

$$\lim_{\beta\to 0} (\beta F_\beta + \ell n Q_\beta) = 0. \tag{61}$$

This equation (61) has not been quoted so far by any author of statistical mechanics in addition to the following Bloch equation:[15]

$$(\partial_\beta + H) U_\beta = 0, \quad U_\beta \overset{\text{def.}}{=} (2\pi)^{3N/2} \langle \vec{r} | e^{-\beta H} | \vec{k} \rangle , \tag{62}$$

which is also derivable from Eq. (60).

The combination of Eq. (59) with Eq. (51) gives our following final form of Neumann's density operator to be used in our later theory:

$$D_\beta = e^{\beta(F_\beta - H)} \quad . \tag{63}$$

This is a more useful form than Eq. (51) since it contains automatically, within it, also a bridge equation, and plays the most central role in modern quantum-statistical mechanics of equilibrium system.

We have, thus, arrived very naturally at the conception of Neumann's density operator, i.e. the most powerful basis of modern quantum-statistical mechanics with one hypothesis, i.e. the law of large numbers, starting from two basic postulates of Schrödinger-Heisenberg's quantum mechanics, i.e. the Schrödinger's time-dependent equation of motion and Born's physical interpretation of wave ket vector $|;t\rangle$. In this way, we could avoid the obscure conception of "the statistical weight" which was first used by Neumann himself and still by other recent authors in formulating Neumann's density operator.[4,6,11,16,17] A further analysis about this operator can be seen in the quoted paper (7).

2.3. The Identical, Indistinguishable Particle System and the Symmetrization of Neumann's Density Matrix

We shall, in this section at first, for our preliminary knowledge of the symmetrization of Neumann's density matrix, present the general quantum-mechanical character of a system of identical, indistinguishable particles of N in number in a different way from those presented by recent authors by using the properties of symmetric group as our mathematical tool.

The system composed of identical, indistinguishable particles is essentially a quantum-mechanical system, of which the generic position, momentum, and spin operators $(\vec{R},\vec{P},\vec{\Sigma})$ corresponding to the so-called "generic distributions"[13],(AII) of them in 3N-dimensional configuration spaces of position, momentum, and spin respectively are commutable every permutation operator Π, i.e.

$$[\vec{R},\Pi] = 0,\ [\vec{P},\Pi] = 0,\ [\vec{\Sigma},\Pi] = 0,\ ^{(AII)} \tag{64}$$

so that the Hamiltonian operator H of the system is commutable also with Π, i.e.

$$[H,\Pi] = 0. \tag{65}$$

The system of identical, indistinguishable particles is to be defined by Eq. (64) instead of Eq. (65), since the system must remain unchanged for the exchange of any two particles which is equivalent physically to the exchange of every observable (including even the observables not commutable with H) concerned with any two particles. As is well-known

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[13] See p 136 of the quoted book 34.

in group theory, every permutation operator Π with the same degree forms together a group which is called the symmetric group, or the permutation group. We denote this group by a symbol $\Phi(N)$. The group $\Phi(N)$ corresponding to the system of N identical, indistinguishable particles has N! order and N degree, and is not abelian. The number $C(N)$ of distinct classes of this group $\Phi(N)$ is equal to the number of distinct positive-integer solutions to the following equation:

$$\sum_{j=1}^{N} jx_j = N. \tag{66}$$

This equation implies that a positive integer N is decomposed into x_1 parts of 1, x_2 parts of 2, x_3 parts of 3, ... , and x_N parts of N. A. Young and G. Frobenius called the numbers $(x_1,x_2,x_3,\ldots,x_N)$ "the partition of positive integer N." Some author represents this structure of partition of positive integer N by a symbole:

$$\left\{1^{x_1},2^{x_2},3^{x_3},\ldots,N^{x_N}\right\}.$$

It is very convenient to use the so-called Young Tableaux in the study of the group $\Phi(N)$ with the degree N not so large.

The order m_i (the number of distinct elements) of the ith class C_i corresponding to the partition:

$$\left\{1^{x_1^{(i)}},2^{x_2^{(i)}},3^{x_3^{(i)}},\ldots,N^{x_N^{(i)}}\right\}$$

is given by

$$m_i = N!\Big/\prod_{j=1}^{N}\left(j^{x_j^{(i)}}\, x_j^{(i)}!\right), \tag{67}$$

[18]

and the total number of elements contained in C(N) classes must be equal to the order of the symmetric group $\Phi(N)$, i.e.

$$\sum_{i=1}^{C(N)} m_i = N! \tag{68}$$

The particularly important knowledge in connection with quantum-statistical mechanics is, as will be seen in a later section, the property of the group $\Phi(N)$ that every element belonging to the same class has the same cyclic structure of permutation and vice versa.

Any permutation of degree N is a product of commuting cycles, and this decomposition is unique. Therefore, every element of the group $\Phi(N)$ can be completely defined by (a) its cyclic structure, i.e. the number of its cycles and their respective lengths, and (b) the numbers appearing each cycle and their order to within a circular permutation. If we reverse the order of the numbers in each cycle, we obtain the inverse element, i.e. the inverse permutation. Every cycle of a given length ℓ is equal to the product of $(\ell-1)$ transpositions, so that any permutation can be decomposed into a product of transpositions. This decomposition is not unique, but the number of transpositions involved will have a definite parity, either even or odd which we shall denote $(-1)^{\Pi}$. A permutation Π is called even, or odd according to $(-1)^{\Pi} = +1$, or -1.

Let Π_{ij} be a transposition operator exchanging #i and #j particles of the system. It is, then, evident that

$$\Pi_{ij}^{-1} = \Pi_{ji} = \Pi_{ij}, \quad \Pi_{ij}^{2} = I \text{ (identity)} \tag{69}$$

so that the eigenvalues of Π_{ij} are +1 and -1.

Every element of the group $\Phi(N)$ must, at least, be unitary, i.e.

$$\Pi^{\dagger}\Pi = \Pi\Pi^{\dagger} = I, \tag{70}$$

since for an arbitrary eigenket $|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle$ of the generic position-operator $\vec{R}$ of the system, we must have, from

$$\Pi|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle \equiv |\Pi\vec{r}_1,\Pi\vec{r}_2,\ldots,\Pi\vec{r}_N\rangle ,$$

that

$$\langle\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N|\Pi^{\dagger}\Pi|\vec{r}'_1,\vec{r}'_2,\ldots,\vec{r}'_N\rangle$$

$$= \langle\Pi\vec{r}_1,\Pi\vec{r}_2,\ldots,\Pi\vec{r}_N|\ \Pi\ \vec{r}'_1,\Pi\vec{r}'_2,\ldots,\Pi\vec{r}'_N\rangle$$

$$= \prod_{\lambda=1}^{N}\delta(\Pi\vec{r}_\lambda-\Pi\vec{r}'_\lambda) = \prod_{\lambda=1}^{N}\delta(\vec{r}_\lambda-\vec{r}'_\lambda) = \langle\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N|\vec{r}'_1,\vec{r}'_2,\ldots,\vec{r}'_N\rangle$$

$$\therefore\quad \Pi^{\dagger}\Pi = I.$$

Among N! permutations contained in the group $\Phi(N)$, N!/2 permutations are even, and the remaining N! permutations are odd. These even permutations form together an invariant subgroup(called the alternating group) of order N!/2 of the group $\Phi(N)$, while odd permutations of N!/2 in number do not since the product of any two odd permutations is even and the identity(an even permutation) is not contained in them.

Since the Hamiltonian operator of the system is invariant under the group operations of $\Phi(N)$ according to Eq. (65), i.e.

$$[H,\Phi(N)] = 0, \tag{71}$$

the symmetric group $\Phi(N)$ belongs to a Schrödinger group so that the state vector must be chosen to be also the eigenket of every element of the group $\Phi(N)$. This implies that the representatives of the state

vector in $\vec{r}$-representation must be completely symmetric since the group $\Phi(N)$ contains every kind of possible exchange pattern of N particles in it. Therefore, we introduce the following operator S constructed from the linear combination of all elements of the symmetric group $\Phi(N)$:

$$S \overset{\text{def.}}{\equiv\equiv} S_{\pm} \overset{\text{def.}}{\equiv\equiv} \frac{1}{N!}\sum_{\Pi} (\pm)^{\Pi}\Pi \quad , \tag{72}$$

where S is the compound operator of two operators S_+ and S_- defined by

$$S_+ \overset{\text{def.}}{\equiv\equiv} \frac{1}{N!}\sum_{\Pi}\Pi, \quad S_- \overset{\text{def.}}{\equiv\equiv} \frac{1}{N!}\sum_{\Pi} (\pm 1)^{\Pi}\Pi \tag{73}$$

with the summation over all N! elements of the group $\Phi(N)$. As we will see immediately, the operator S plays a role of symmetrizing completely every vector to which it is applied. This situation may be seen also as follows:

Let $|\rangle$ be an arbitrary ket-vector, and $|\rangle'$ be the ket-vector produced by applying the operator S on $|\rangle$, i.e.

$$|\rangle' = S\,|\rangle. \tag{74}$$

Now, let us apply an arbitrary element Π' of the group $\Phi(N)$ on the ket-vector $|\rangle'$. We see, then,

$$\Pi'|\rangle' = \Pi' S|\rangle = \frac{1}{N!}\sum_{\Pi} (\pm 1)^{\Pi}\Pi'\Pi|\rangle$$

$$= \frac{(\pm 1)^{\Pi'}}{N!}\sum_{\Pi} (\pm 1)^{\Pi''}\Pi''|\rangle = (\pm 1)^{\Pi'} S|\rangle = (\pm)^{\Pi'}|\rangle'$$

$$\therefore \qquad \Pi'|\rangle' = (\pm)^{\Pi'}|\rangle', \text{ or } \Phi(N)|\rangle' = (+, \text{ or } -)|\rangle', \tag{75}$$

[14] The sign "+" corresponds to the operator S_+, and the sign "−" corresponds to the operator S_-.

by noting the group property of $\Phi(N)$, i.e. the combination of two elements Π' and Π must be an element of the group $\Phi(N)$ with changing the original parity $(\pm 1)^{\Pi}$ into its own parity $(\pm 1)^{\Pi''}$ multiplies by $(\pm 1)^{\Pi'}$. Equation (75) shows us that the ket-vector $|\rangle'$ obtained by the operation of the operator S on $|\rangle$ as in Eq. (74) remains unchanged within its sign by the operation of the group $\Phi(N)$. This implies that the ket-vector $|\rangle'$ is completely symmetric, or antisymmetric for every possible exchange pattern of N particles in the system under consideration. In this sense, we call the operator S_+ the complete symmetrizer, and the operator S_- the complete antisymmetrizer.

We see easily that the following properties of the compound operator S of the complete symmetrizer S_+ and antisymmetrizer S_-:

$$S^{\dagger} = S, \quad S^2 = S, \tag{76}$$

and

$$\Pi(S_+,S_-) = (S_+,S_-)\Pi = (S_+,(-1)^{\Pi}S_-) \quad . \tag{77}$$

Equation (71) leads, furthermore, to

$$[S,H] = 0, \tag{78}$$

that is, the operator S is a constant of motion, and Eq. (76) shows us that the operator S can be regarded as an Hermitian projection operator(idempodent):

$$S = S^n, \quad (n=2,3,4,\ldots). \tag{79}$$

We have also

$$S_+S_- = S_-S_+ = 0. \tag{80}$$

Since the generic position- and spin-operators of the system are commutable with an arbitrary permutation operator Π as discussed already in Eq. (64), they are commutable also with the symmetric group $\Phi(N)$, i.e.

$$[\vec{R},\Phi(N)] = 0. \tag{81}$$

so that

$$[\vec{R},S] = 0.^{15} \tag{82}$$

Equation (82) implies that there must be simultaneous eigenket vectors between $\vec{R}$ and S. Let $|\vec{r}\rangle$ be one of these simultaneous eigenket vectors, i.e.

$$\vec{R}|\vec{r}\rangle = \vec{r}|\vec{r}\rangle \ , \quad S|\vec{r}\rangle = s|\vec{r}\rangle \ . \tag{83}$$

The eigenvalue s of S can, by using Eq. (76), be found easily as follows:

$$s^2|\vec{r}\rangle = S^2|\vec{r}\rangle = S|\vec{r}\rangle = s|\vec{r}\rangle \ ,$$

$$\therefore \quad s^2 - s = 0, \quad \therefore \quad s = 0, \ 1. \tag{84}$$

This is trivial according to the general character of idempodent since the complete symmetrizer S is an idempodent. We note here that for symmetrizer S_+ the eigenkets corresponding to s = 1,0 are symmetric and antisymmetric, and for antisymmetrizer S_-, vice versa respectively.

We are now interested only in the eigenket $|\vec{r}\rangle$ corresponding to the eigenvalue s = 1, i.e.

$$S|\vec{r}\rangle = |\vec{r}\rangle \ . \tag{85}$$

One of the eigenkets of the generic position-operator $\vec{R}$ is

$$\vec{R}|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle = \vec{r}|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle$$

but this eigenket $|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle$ is not the simultaneous eigenket of the of the compatible symmetrizer S with $\vec{R}$. Now, let us apply the group

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[15] We symbolize totally the generic position- and spin-operators by one notation $\vec{R}$ this time on, so that the eigenvalue of $\vec{R}$ contains also the spin coordinates.

operation $\Phi(N)$ on this eigenvalue equation by noting Eq. (81). We see then that

$$\vec{R}(\Phi(N)|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle) = \vec{r}(\Phi(N)|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle) \quad ,$$

so that the N! ket vectors given by

$$\Phi(N)|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle \tag{86}$$

are also the eigenkets of $\vec{R}$ belonging to the same eigenvalue $\vec{r}$. Furthermore they are linearly independent of each other since we have for the Hermitian scalar product of two arbitrary members of Eq. (86),

$$\langle\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N|\Pi^{\dagger}\Pi'|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle = \prod_{j=1}^{N}\delta(\vec{r}_j-\Pi''\vec{r}_j)$$

by using the group property of $\Phi(N)$ and Eq. (77) of the unitary property of Π, where $\Pi'' = \Pi^{-1}\Pi'$. We may say thus that a continuous eigenvalue $\vec{r}$ of the generic position-operator $\vec{R}$ is N!-fold degenerate with N! eigenkets given by Eq. (86). This means physically that we have N! possible ways of distributing N particles of the system for one generic distribution chosen. Therefore, we make, according to the ususal procedure used in quantum mechanics, a linear combination of these N! eigenkets of Eq. (86) to give the simultaneous eigenket of the completely symmetrizing operator S. It is as follows:

$$|\vec{r}\rangle = \sum_{\Pi}\frac{(\pm1)^{\Pi}}{N!}\Pi|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle \quad ,$$

which is written actually in the following form:

$$|\vec{r}\rangle = S|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle \tag{87}$$

by using the definition given by Eq. (72). The proof showing that Eq. (87) is the eigenket of S corresponding to its eigenvalue 1 among two possible values is, by using Eq. (76), done simply as follows:

$$S|\vec{r}\rangle \equiv S^2|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle = S|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle \quad ,$$

or

$$S|\vec{r}\rangle = |\vec{r}\rangle \ .$$

We have not discussed, so far, the applications of the complete symmetrizer S_+ and antisymmetrizer S_- for our physical theory. However, it has turned out that the operator S_+ can be used for the symmetrization applicable to a bason-system, while the operator S_- can be used for the antisymmetrization applicable to a fermion-system.(19) We will distinguish hereafter every physical object concerned with a boson-system and a fermion-system to be needed in our further theory by using the subscripts, or superscripts, "+" and "−" respectively, i.e. the subscripts, or superscripts, "+" stands for a boson-system, and "−", for a fermion-system.

Our above theory leads us to the generic position-ket vector,

$$\begin{bmatrix} |\vec{r}\rangle_+ \\ |\vec{r}\rangle_- \end{bmatrix} = \begin{bmatrix} S_+ \\ S_- \end{bmatrix} |\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle \ , \tag{88}$$

and similarly, for the generic momentum-, or propagation-ket vector,

$$\begin{bmatrix} |\vec{k}\rangle_+ \\ |\vec{k}\rangle_- \end{bmatrix} = \begin{bmatrix} S_+ \\ S_- \end{bmatrix} |\vec{k}_1,\vec{k}_2,\ldots,\vec{k}_N\rangle . \tag{89}$$

The Hermitian scalar product between two eigenket vectors of the compound form S of two kinds of symmetrizers S_+ and S_- is, by using Eq. (76), given by

$$\langle\vec{r}|\vec{r}'\rangle_\pm \overset{\text{def.}}{=\!=} \delta(\vec{r},\vec{r}') = \frac{1}{N!}\sum_{\Pi}(\pm 1)^{\Pi}\left[\prod_{j=1}^{N}\delta(\vec{r}_j - \Pi\vec{r}_j)\right] . \tag{90}$$

Since the ket vector $|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle$ may be regarded as a simultaneous eigenket vector of N commutable indivitual-operators $\vec{R}_j$ (j=1,2, ...,N), this ket vector can be decomposed into direct products of N indivitual eigenket vectors of $\vec{R}_j$ given by

$$|\vec{r}_j\rangle_j,\ (j=1,2,\ldots,N)\ ^{16}\ ,$$

that is,

$$|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle = |\vec{r}_1\rangle_1|\vec{r}_2\rangle_2\ \ldots\ldots|\vec{r}_N\rangle_N\ . \tag{91}$$

At this point, it should be mentioned that we should distinguish substantially the two possible kinds of permutation operators Π and $\mathcal{P}$, in which the former Π is the permutation operator permuting the order of N indivitual particles and the latter $\mathcal{P}$ is the permutation operator permuting the order of N indivitual eigenket vectors, so that it should be

$$\left.\begin{aligned} &\Pi|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle \neq |\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle\ ,\ (\Pi\neq I)\ ,\\ &\mathcal{P}|\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle = |\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle\ ,\\ &\text{and, likewise, we have}\\ &\Pi|\vec{k}_1,\vec{k}_2,\ldots,\vec{k}_N\rangle \neq |\vec{k}_1,\vec{k}_2,\ldots,\vec{k}_N\rangle\ ,\ (\Pi\neq I),\\ &\mathcal{P}|\vec{k}_1,\vec{k}_2,\ldots,\vec{k}_N\rangle = |\vec{k}_1,\vec{k}_2,\ldots,\vec{k}_N\rangle\ . \end{aligned}\right\}^{7,12} \tag{92}$$

The combination of Eq. (91) with Eq. (87) makes us see the following

---

[16] We note here that we are concerned necessarily with writing the subscript j on these N indivitual eigenket vectors for the distinguishability of N indivitual eigenket vectors coming from the distinguishability of N particle's positions still remained, i.e. $\vec{R}_j|r_\lambda\rangle_j = r_\lambda|r_\lambda\rangle_j$ for the jth position operator within the generic position operator $\vec{R}$.

alternant forms of two eigenket vectors $|\vec{r}\rangle$ and $|\vec{k}\rangle$ of the generic position- and propagation-operators:

$$|\vec{r}\rangle_{\pm} = \frac{1}{N!} \begin{vmatrix} |\vec{r}_1\rangle_1 & |\vec{r}_2\rangle_1 & \cdots\cdots & |\vec{r}_N\rangle_1 \\ |\vec{r}_1\rangle_2 & |\vec{r}_2\rangle_2 & \cdots\cdots & |\vec{r}_N\rangle_2 \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ |\vec{r}_1\rangle_N & |\vec{r}_2\rangle_N & \cdots\cdots & |\vec{r}_N\rangle_N \end{vmatrix}_{\pm} ,$$

or in an abbreviated form:

$$|\vec{r}\rangle_{\pm} = \frac{1}{N!} \left| |\vec{r}_i\rangle_j \right|_{\pm} \tag{93}$$

similarly,

$$|\vec{k}\rangle_{\pm} = \frac{1}{N!} \left| |\vec{k}_i\rangle_j \right|_{\pm} \tag{94}$$

which are formally similar to the so-called Slater determinant (or permanant) with a different realistic meaning.[7,20]

All of above basic discussions lead us to a conclusion that the state-ket vector $|;t\rangle$ of a system of identical, indistinguishable particles must, in the configuration representation, given by

$$\langle \vec{r}|;t\rangle_{\pm} = \langle \vec{r}_1, \vec{r}_2, .., \vec{r}_N|S|;t\rangle$$

$$= \frac{1}{N!} \sum_{\Pi} (\pm 1)^{\Pi} \langle \Pi r_1, \Pi r_2, \ldots, \Pi r_N|;t\rangle , \tag{95}$$

and, in the momentum or propagation representation,

$$\langle k|;t\rangle_{\pm} = \langle k_1, k_2, \ldots, k_N|S|;t\rangle$$

$$= \frac{1}{N!} \sum_{\Pi} (\pm 1)^{\Pi} \langle \Pi k_1, \Pi k_2, \ldots, \Pi k_N|;t\rangle , \tag{96}$$

which can be extended to that of any representation.

We are, now with the preliminary knowledge discussed above, in a position to have the symmetrization of the representatives of Neumann's density operator in a representation. As shown already, this density operator has the form given by Eq. (63), i.e. a negatively exponential operator-function of single operator-variable H which is the Hamiltonian operator of the system under consideration, and Eqs. (78) and (71) show us that

$$[\Phi(N),D_\beta] = 0, \quad [S,D_\beta] = 0. \tag{97}$$

Equation (97) requires that the representatives $D_\beta(\vec{r},\vec{r}')$ defined by

$$D_\beta(\vec{r},\vec{r}') \overset{\text{def}}{=\!=} \langle \vec{r}|D_\beta|\vec{r}'\rangle \tag{98}$$

must be symmetric, or antisymmetric under the symmetric group operation $\Phi(N)$ in the system of identical, indistinguishable particles. This requirement forces us to use the symmetrized representation $|\vec{r}\rangle$ in Eq. (98). We have, thus by combining Eq. (98) with the symmetrized representation $|\vec{r}\rangle$ given by Eq. (87),

$$D_\beta(\vec{r},\vec{r}') = e^{\beta F_\beta}\langle \vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N|S^{\dagger}e^{-\beta H}S|\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N'\rangle ,$$

which is, by using the second of Eq. (97) and Eq. (76), reduced to a simpler form given by

$$D_\beta(\vec{r},\vec{r}') = e^{\beta F_\beta}\langle \vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N|e^{-\beta H}S|\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N'\rangle . \tag{99}$$

Similarly, we have, in $\vec{k}$-representation,

$$D_\beta(\vec{k},\vec{k}') = e^{\beta F_\beta}\langle \vec{k}_1,\vec{k}_2,\ldots,\vec{k}_N|e^{-\beta H}S|\vec{k}_1',\vec{k}_2',\ldots,\vec{k}_N'\rangle . \tag{100}$$

Likewise, we can construct also the representatives of Neumann's density operator in any representation other than $\vec{r}$-, or $\vec{k}$-representation according to our convenience for the practical purpose with which we are concerned. However, the form given by Eq. (99) is most preferable since the potential function contained in the Hamiltonian operator H is, in the most cases of realistic problems, given by a complicated form in terms of the coordinate $(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ of the representative point of the system in 3N-dimensional configuration space.

Now, we introduce the following notation to avoid duplicate writings in our subsequent discussions:

$$|\vec{r}'s\rangle \overset{\text{def.}}{\equiv} |\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N\rangle; \quad |\vec{k}'s\rangle \overset{\text{def.}}{\equiv} |\vec{k}_1,\vec{k}_2,\ldots,\vec{k}_N\rangle.$$

Let us, for example, insert the identity operator I taking the form given by

$$I \equiv \int_{\infty} d^{3N}\vec{k}\,|\vec{k}'s\rangle\langle\vec{k}'s| \tag{100}$$

between two operators $\exp(-\beta H)$ and S in Eq. (99), to have the following expression of diagonal element convenient for a practical calculation:

$$D_{\beta}^{\pm}(\vec{r},\vec{r}) = \frac{\exp(\beta F_{\beta}^{\pm})}{(2\pi)^{3N}N!}\sum_{\Pi}(\pm 1)^{\Pi}\int_{\infty} d^{3N}\vec{k}\, e^{-i(\Pi\vec{k})\cdot\vec{r}}\, e^{-\beta H(-i\hbar\vec{\nabla},\vec{r})}\, e^{i\vec{k}\cdot\vec{r}} \ldots \tag{101}$$

by using

$$\langle\vec{r}'s|\vec{k}'s\rangle \equiv e^{i\vec{k}\cdot\vec{r}}/(2\pi)^{3N/2}, \tag{102}$$

where the superscript "+" stands for Boson-system, while "−" for Fermion-system as stated already, and we note here that

$$(\Pi\vec{k})\cdot\vec{r} = \vec{k}\cdot(\Pi\vec{r}) \tag{103}$$

in accordance with the unitary character of every element of the symmetric group $\mathfrak{S}(N)$.

As shown in Eq. (101), the explicit determination of Neumann's density matrix $D_\beta^{\pm}(\vec{r},\vec{r}')$ is dependent upon finding the explicit function obtained by operating out the operator $\exp(-\beta H)$ on the function $\exp(i\vec{k}\cdot\vec{r})$, i.e.

$$e^{-\beta H(-i\hbar\vec{\nabla},\vec{r})}e^{i\vec{k}\cdot\vec{r}} \tag{104}$$

in addition to the completion of the given integral in $\vec{k}$-space, which compels us to define the so-called Bloch function $U_\beta(\vec{k},\vec{r})$ given by Eq. (62). We shall return to this problem again in Chapter III.

2.4. A New Formal Expansion Theory of the Quantum Partition Function of Canonical Ensemble

We are, in this section, interested in developing a new formal expansion theory of the quantum partition function Q_β using the characters of symmetric group $\mathfrak{S}(N)$ within the framework of our fundamental theory of quantum statistical mechanics. As well known, this partition function Q_β plays a role of a bridge between the microscopic and macroscopic worlds, and also between canonical and grand canonical ensembles. This function Q_β is found from the normalization character of the trace of Neumann's density operator D_β stated in Eq. (53) already. Physically, this normalization character implies the following meaning: Let us suppose that a quantum-mechanical system composed of N identical particles is closed in a volume V which is in contact with an isothermal bath. It is, then, evident that every particle can be found quite certainly in the volume V. The trace of the density matrix $D_\beta(\vec{r},\vec{r}')$

must, therefore, be normalized for the integration over the 3N-dimensional domain V^N in the 3N-dimensional configuration space of the system in question, i.e.

$$\int_{V^N} d^{3N}\vec{r}\,\langle\vec{r}|D_\beta|\vec{r}\rangle = 1, \tag{105}$$

which leads us to have the same result as Eq. (53).

For our later reference, we shall start with deriving the so-called quasi-quantum partition function $Q_\beta^{(0)}$ of the system of N identical particles. The generic position-eigenket vector $|\vec{r}\rangle$ is, for the system of identical, distinguishable particles, given simply by the direct product of the indivitual position-eigenket vectors, i.e.

$$|\vec{r}\rangle = \prod_{j=1}^{N} |\vec{r}_j\rangle \equiv |\vec{r}'s\rangle \ . \tag{106}$$

The substitution of Eq. (106) into Eq. (53) give us

$$\begin{aligned} Q_\beta^{(0)} &= \int_{V^N} d^{3N}\vec{r}\,\Big(\prod_{i=1}^{N} \langle\vec{r}_i|\Big)\, e^{-\beta H}\Big(\prod_{j=1}^{N} |\vec{r}_j\rangle\Big) \\ &= \int_{V^N} d^{3N}\vec{r}\,\langle\vec{r}'s|e^{-\beta H}|\vec{r}'s\rangle \ . \end{aligned} \tag{107}$$

Equation (107) is the quasi-quantum partition function corresponding to the original Maxwell-Boltzmann statistics. On the other hand, the quasi-quantum partition function $Q_\beta^{(0)}$ corresponding to the corrected Maxwell-Boltzmann statistics is given by

$$Q_\beta^{(0)} = Q_\beta^{(c)}/N! \tag{108}$$

according to Gibb's intuitive foresight which is even incorrect under the point of view of modern quantum mechanics.

If the identical particles of the system are independent, i.e. there is no interaction between particles, the total Hamiltonian operator H of the system is split into the sum of the individual Hamiltonian operators $h_j (j=1,2,\ldots,N)$, i.e.

$$H = \sum_{j=1}^{N} h_j \quad ,$$

and Eq. (108) is, then, given by

$$Q_\beta^{(c)} = q_\beta^N/N! \quad , \quad q_\beta \overset{\text{def.}}{=\!=} \int_\infty d^3\vec{x}\langle\vec{x}|e^{-\beta h}|\vec{x}\rangle, \tag{109}$$

where the determination of the individual partition function q_β belongs to the problem of single particle. If the single particle is structureless, the operator h takes simply the following form:

$$h = -\frac{\hbar^2}{2m}\nabla^2 \quad ,$$

where m is the mass of single particle. For the particle with an inner structure, we need to solve the Schrödinger's time-independent equation of single particle given by

$$h|n\rangle = \mathcal{E}_n|n\rangle \quad ,$$

and we calculate, then, the function q_β in the way like

$$q_\beta = \sum_n \int_\infty d^3\vec{x}\langle\vec{x}|n\rangle\langle n|e^{-\beta h}|\vec{x}\rangle = \sum_n e^{-\beta\mathcal{E}_n} \tag{110}$$

by using the identity operator constructed from the complete set $\{|n\rangle\}$ of Hamiltonian eigenket vectors of single particle.

Now, we introduce the quantum partition function Q_β. This is done by combining the symmetrized eigenket vector $|\vec{r}\rangle$ of generic

position-operator $\vec{R}$ given by Eq. (87) with Eq. (53). We have, thus,

$$Q_\beta \equiv e^{-\beta F_\beta} = \int_{V^N} d^{3N}\vec{r} \langle \vec{r}'s | e^{-\beta H} s | \vec{r}'s \rangle, \tag{111}$$

or

$$Q_\beta^\pm \equiv e^{-\beta F_\beta^\pm} = \frac{1}{N!} \sum_\Pi (\pm 1)^\Pi \int_{V^N} d^{3N}\vec{r} \langle \vec{r}'s | e^{-\beta H_\Pi} | \vec{r}'s \rangle \ , \tag{112}$$

by using Eq. (72). The summation in Eq. (112) runs over all the N! elements contained in the symmetric group $\Phi(N)$. We rearrange this summation in such a way that every term of Eq. (112) belonging to the same class of the group $\Phi(N)$ is collected together. Before doing this, we examine the simplest solution to Eq. (66). It is

$$x_1 = N, \quad x_j = 0, \ (j=2,3,\ldots N),$$

which leads to the following cyclic structure:

$$\{1^N, 2^0, 3^0, \ldots, j^0, \ldots, N^0\},$$

and the number m_1 of distinct elements contained in the class with this cyclic structure is, in accordance with Eq. (67), given by

$$m_1 = 1,$$

i.e. only one element. This is nothing but the identity I which forms by itself a subgroup and a class of the group $\Phi(N)$. Since the parity $(\pm 1)^{p_i}$ of the ith class C_i with the cyclic structure given by

$$\{1^{x_1^{(i)}}, 2^{x_2^{(i)}}, 3^{x_3^{(i)}}, 4^{x_4^{(i)}}, \ldots, N^{x_N^{(i)}}\}, \tag{113}$$

is, in general, determined by the positive integer p_i given by

$$p_i = x_2^{(i)} + x_4^{(i)} + x_6^{(i)} + \ldots + x_{2j}^{(i)} + \ldots, \ (21) \tag{114}$$

the parity $(\pm 1)^{p_1}$ of this class is

$$p_1 = 0+0+ \ldots = (\text{even}) \quad .$$

We call, hereafter, this simplest class the first class of the group $\Phi(N)$.

We put, thus, the term corresponding to this first class at the first place in the rearrangement of all terms of Eq. (112). We have then,

$$Q_\beta^{\pm} = \frac{1}{N!}\int_V^{3N}\vec{r}\langle \vec{r}', s|e^{-\beta H}|\vec{r}', s\rangle + \frac{1}{N!}\sum_{i=2}^{C(N)}\left[\,(\pm 1)^{p_i}\sum_{\lambda=1}^{m_i} J_i^{\lambda}\,\right], \tag{115}$$

where the summation inside of $[\,\cdots\,]$ represents the total sum of integrals J_i^{λ} defined by

$$J_i^{\lambda} \overset{\text{def.}}{=\!=} \int_V^{3N}\vec{r}\langle \vec{r}', s|\Pi_i^{\lambda} e^{-\beta H}|\vec{r}', s\rangle \tag{116}$$

corresponding to all elements $\Pi_i^{\lambda}, (\lambda = 1,2,3,\ldots,m_i)$, of the ith class C_i with the parity determined by the positive integer p_i of Eq. (114), and $C(N)$ is the total number of classes of the group $\Phi(N)$.

Now, we are going to prove that the integral J_i^{λ} defined by Eq. (116) does not depend upon the superscript λ but only the subscript i. In another word, the integrals $J_i^{\lambda}(\lambda = 1,2,\ldots,m_1)$ corresponding to the permutations $\Pi_i^{\lambda}(\lambda = 1,2,\ldots,m_i)$ belonging to the same class C_i are all the same. The proof for this is as follows:

Let $\Pi_i^{\lambda}(\lambda = 1,2,\ldots,m_i)$ be in the same class C_i. Then, there must be such elements $\textcircled{H}_i^{\lambda}, (\lambda = 1,2,\ldots,m_i)$ that

$$\Pi_i^{\lambda} = \left(\textcircled{H}_i^{\lambda}\right)^{\dagger}\,\Pi_i\,\textcircled{H}_i^{\lambda}\,, (\lambda\ 1,2,\ldots,m_i),$$

in accordance with the definition of class, and the element $\textcircled{H}_i^{\lambda}$ is unitary in accordance with Eq. (76). Furthermore, it, or its Hermitian conjugate is commutable with the operator exp(-βH) in accordance with Eq. (65). These characters of $\textcircled{H}_i^{\lambda}$ lead to

$$\langle \vec{r}'s|\Pi_i^{\lambda} e^{-\beta H}|\vec{r}'s\rangle = \langle \textcircled{H}_i^{\lambda}\vec{r}'s|\Pi_i' e^{-\beta H}|\textcircled{H}_i^{\lambda}\vec{r}'s\rangle,$$

and

$$d^{3N}\vec{r} = d^{3N}(\textcircled{H}_i^{\lambda}\vec{r}).$$

Therefore, the integral given by Eq. (116) is written also as

$$J_i^{\lambda} = \int_{V^N} d^{3N}(\textcircled{H}_i^{\lambda}\vec{r})\langle \textcircled{H}_i^{\lambda}\vec{r}'s|\Pi_i' e^{-\beta H}|\textcircled{H}_i^{\lambda}\vec{r}'s\rangle$$

$$= \int_{V^N} d^{3N}\vec{r}'\langle \vec{r}''s|\Pi_i' e^{-\beta H}|\vec{r}''s\rangle$$

by putting $\vec{r}' \equiv \textcircled{H}_i^{\lambda}\vec{r}$, which is equal to the integral J_i', i.e.

$$J_i^{\lambda} = J_i', (\lambda=2,3,..,m_i). \tag{117}$$

This shows us that the integral J_i^{λ} defined by Eq. (116) is independent of the superscript λ. We substitute Eq. (117) into Eq. (115), and then use Eq. (67) to have

$$Q_{\beta}^{\pm} = \frac{1}{N!}\int_{V^N} d^{3N}\vec{r}\langle \vec{r}'s|e^{-\beta H}|\vec{r}'s\rangle$$

$$+ \sum_{i=2}^{C(N)} (\pm 1)^{pi}\left[\prod_{j=1}^{N} x_j^{(i)} \cdots x_j^{(i)}\right]^{-1} J_i \tag{118}$$

with

$$J_i \overset{\text{def.}}{\equiv} \int_{V^N} d^{3N}\vec{r}\langle \vec{r}'s|\Pi_i' e^{-\beta H}|\vec{r}'s\rangle, \tag{119}$$

where Π_i' is any one permutation-operator among all elements belonging to the ith class C_i of the symmetric group $\mathfrak{S}(N)$.[17]

We call this expansion of Eq. (118) the symmetric-group-class expansion formula for the quantum partition function of canonical ensemble. The quasi-quantum partition function $Q_\beta^{(c)}$ given by Eq. (108) and corresponding to the corrected Maxwell-Boltzman statistics appears as the first class term in our expansion formula of Eq. (118), which does not make the distinction between a boson and fermion on their specific behaviors. This distinction is first seen in the second class term. It is supposed that this second class term plays a main role in the quantum-effect due to the spin-characteristics of indivitual particle since the other class terms of the expansion with more complicated cyclic structure than that of this second class term may be considered to be quite small in their numerical contributions to the function Q_β at a temperature different from zero.

As Eq. (118) shows us that the quantum partition function Q_β may be regarded as the superposition of every partition function $Q_\beta^{(i)}$(i=1,2, 3,...,C(N)) belonging to every indivitual class C_i(i=1,2,3,..,C(N)) of the symmetric group $\mathfrak{S}(N)$, i.e.

$$Q_\beta = \sum_{i=1}^{C(N)} Q_\beta^{(i)} \quad . \tag{120}$$

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[17] It is a very much impressed fact that the cyclic structure of Π_i' is equivalent to the structure of irreducible cluster integral in the Mayer's classical theory. We may call the integral J_i the quantum irreducible cluster integral in analogy with the classical nomenclature. We may apply the Mayer's cluster theory to our expansion theory.

This decomposition of Q_β into its components is unique since a symmetric group with a given degree and therefore a given order determines uniquely the structures of its classes, and the number C(N) of total components of Q_β is equal to the number of distinct classes, i.e. the number of inequivalent irreducible representations of the symmetric group. In other words, the components of Q_β given by

$$(Q_\beta^{(1)}, Q_\beta^{(2)}, \ldots, Q^{(C(N))})$$

have one-to-one correspondences to the inequivalent irreducible representations of the symmetric group corresponding to the system under consideration. In this sense, our expansion theory of the quantum partition function is considered to be reasonable from the group-theoretical point of view.

There are two kinds of jobs to determine our quantum partition functions Q_β exactly, i.e.

(a) the complete determination of (C(N)-1) numerical coefficients of the integrals J_i(i=2,3,...,C(N)), in addition to the positive integer p_i(i=2,3,...,C(N)) concerned with the parity of the ith class, i.e. to find the solutions of C(N) in number to Eq. (66),

(b) the complete determination of C(N) integrals J_i(i=1,2,...,C(N)), where J_1 is the integral of first class term of expansion in Eq. (118).

Realistically, since we are dealing with the macroscopic system containing a vast number of particles, the number C(N) may be also large enough. According to the Hardy-Ramanujan's asymptotic formula,[22,23]

this number C(N) is, if N→∞, given by

$$C(N) \cong e^{\pi\sqrt{2N/3}}/4\sqrt{3}\,N. \tag{121}$$

We have, for example, for N = 6.02486x10^{23}(gmol)$^{-1}$,

$$C(N) \sim 10^{10^{13}}.$$

We are, therefore, concerned with the determinations of numerical coefficients and integrals of the order of $10^{10^{13}}$ in number respectively in the calculation of Q_β of even one gmol substance. However, as stated somewhat already, the first few class terms of Eq. (118) with simpler cyclic structures would be decisively significant. This makes feasible the solution of the realistic problem with which we are concerned.

We will show below these first few class terms which we have obtained by using the identity of Eq. (100)' constructed from the $\vec{k}$-eigenket vectors $|\vec{k}\rangle$'s.[7] In the use of this identity, the C(N) components of Q_β are given by

$$Q_\beta^{(1)} = Q_\beta^{(c)} = \frac{(1/2\pi)^{3N}}{N!}\int_{V^N} d^{3N}\vec{r} \int_{\infty} d^{3N}\vec{k}\, e^{-i\vec{k}\cdot\vec{r}} e^{-\beta H} e^{i\vec{k}\cdot\vec{r}}, \tag{122}$$

$$Q_\beta^{(i)} = (\pm 1)^{Pi}\left[\prod_{j=1}^{N} x_j^{(i)}\, x_j^{(i)}!\right]^{-1} J_i$$

with

$$J_i \overset{\text{def.}}{=\!=} \int_{V^N} d^{3N}\vec{r} \int_{\infty} d^{3N}\vec{k}\, \langle\vec{k}'s|\Pi_i^1|\vec{r}'s\rangle e^{-\beta H}\langle\vec{r}'s|\vec{k}'s\rangle$$

$$(i=2,3,4,\ldots,C(N)) \quad .$$

We should take the following binary cyclic structure:

$$\left\{1^{N-2},2^1,3^0,\ldots,j^0,\ldots,N^0\right\}$$

corresponding to the second class term $Q_\beta^{(2)}$, of which the coefficient is given by

$$\prod_{j=1}^{N} x_j^{(2)}!\; x_j^{(2)}! = 2[(N-2)!],$$

and the parity integer p_2 is, in accordance with Eq. (114), given by

$$p_2 = 1 + 0 + 0 + \ldots = 1 \quad \text{(odd)} \quad .$$

We have, thus, after a rearrangement,

$$Q_\beta^{(2)} = \pm \frac{(1/2\pi)^{3N}}{2\cdot(N-2)!} \int_V d^{3N}\vec{r} \int_\infty d^{3N}\vec{k}\, e^{i(\vec{k}_1-\vec{k}_2)\cdot(\vec{r}_1-\vec{r}_2)} \boxed{e^{-i\vec{k}\cdot\vec{r}}\, e^{-\beta H}\, e^{i\vec{k}\cdot\vec{r}}} \tag{123}$$

Likewise, we have

$$Q_\beta^{(3)} = \frac{(1/2\pi)^{3N}}{3\cdot(N-3)!} \int_V d^{3N}\vec{r} \int_\infty d^{3N}\vec{k}\, \mathrm{Exp}[i(\vec{k}_1-\vec{k}_2)\cdot\vec{r}_1+i(\vec{k}_2-\vec{k}_3)\cdot\vec{r}_2+i(\vec{k}_3-\vec{k}_1)\cdot\vec{r}_3]$$

$$\times \boxed{e^{-i\vec{k}\cdot\vec{r}}\, e^{-\beta H}\, e^{i\vec{k}\cdot\vec{r}}} \tag{124}$$

Corresponding to the following tenary cyclic structure:

$$\left\{1^{N-3},2^0,3^1,4^0,\ldots,j^0,\ldots,N^0\right\}, p_3 = 0,$$

and, in general, we have

$$Q_\beta^{(j)} = (\pm 1)^{j-1} \frac{(1/2\pi)^{3N}}{j\cdot(N-j)!} \int_V d^{3N}\vec{r} \int_\infty d^{3N}\vec{k}\, \boxed{e^{-i\vec{k}\cdot\vec{r}}\, e^{-\beta H}\, e^{i\vec{k}\cdot\vec{r}}}$$

$$\times \mathrm{Exp}\left[i \sum_{\lambda=1}^{j-1} (\vec{k}_\lambda-\vec{k}_{\lambda+1})\cdot\vec{r}_\lambda + i(\vec{k}_j-\vec{k}_1)\cdot\vec{r}_j\right], \tag{125}$$

corresponding to the following cyclic structure:

$$\left\{1^{N-j},2^{0},3^{0},\ldots,j^{1},\ldots,N^{0}\right\},\ p_j = j-1.$$

In this way, we can determine any kind of desired class term $Q_\beta^{(i)}$.(7)

As we have seen above, the function $F_\beta'(k,r)$ defined by

$$F_\beta'(\vec{k},\vec{r}) \stackrel{\text{def.}}{=} e^{-i\vec{k}\cdot\vec{r}}\, e^{-\beta H}\, e^{i\vec{k}\cdot\vec{r}} \tag{126}$$

with a temperature-boundary condition given by

$$[F_\beta'(\vec{k}\cdot\vec{r})]_{\beta=0} = 1, \tag{127}$$

plays, in some sense, a basic role in the practical determination of $Q_\beta^{(i)}$ (i=1,2,3,...,C(N)) in our expansion theory. This function $F_\beta'(\vec{k}\cdot\vec{r})$ is connected with the function of Eq. (104), or the Bloch function U_β defined by Eq. (62) in the difference of only the pure imaginary exponential function. This function has many interesting but unaccessible characters(7) which give us sometimes even a hopelessness in the concrete solution of a problem of quantum statistical mechanics. We will be confronted with the same problem in our subsequent theory of correlation function in next section.

As our first trial approximation of Q_β, we may take

$$Q_\beta^{\pm} \doteq Q_\beta^{(1)} = Q_\beta^{(c)} \quad . \tag{128}$$

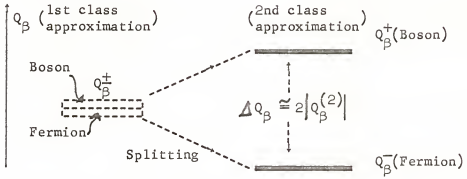
This approximation does not give the distinguishability between the boson and fermion systems. Our next possible approximation is to take

$$Q_\beta^{\pm} \doteq Q_\beta^{(1)} + Q_\beta^{(2)} \ , \tag{129}$$

or in its explicit form:

$$Q_\beta^{\pm} \doteq \frac{(1/2\pi)^{3N}}{N!}\int_{V^N} d^{3N}\vec{r} \int_{\infty} d^{3N}\vec{k} F_\beta'(\vec{k},\vec{r})\left[1 \pm \frac{N(N-1)}{2} e^{i(\vec{k}_1-\vec{k}_2)\cdot(\vec{r}_1-\vec{r}_2)}\right] , \tag{130}$$

where $F'_\beta(\vec{k},\vec{r})$ was defined already by Eq. (126). The different behavior between the boson and fermion systems is seen firstly in this second class-term approximation. The following diagram may give us an aid to distinguish the quantum partition functions Q_β^+ and Q_β^- for a boson and fermion systems:



This situation of splitting due to the exchange effect of particles is, in some sense, similar to the perturbed splitting of energy level due to the orbital-orbital, orbital-spin, spin-spin interactions, the relativistic effect of electrons and other kinds of interactions in an atom. Finally, it should be mentioned that our expansion theory is comparable with Kahn-Uhlehbeck's quantum cluster expansion theory. However, there is a great difference between them ideologically.

2.5. The Formal Theory of Quantum Pair Correlation Function

A diagonal element $D_\beta(\vec{r},\vec{r})$, i.e.

$$D_\beta(\vec{r},\vec{r}) = \langle\vec{r}|D_\beta|\vec{r}\rangle$$

of the Neumann's density matrix given by Eq. (98), is interpreted physically as the probability density of finding the representative point of a quantum-mechanical system of identical, indistinguishable

particles at any one point among all points corresponding to the same generic configuration of the system specified by $(\vec{r}_1\vec{r}_2\vec{r}_3\ldots\vec{r}_N)^{(AII)}$ in 3N-dimensional configuration space. Therefore, the probability density of finding simultaneously any two particles of the system at two points specified by two position-vectors $\vec{r}_1$ and $\vec{r}_2$ in a volume V in realistic space, is given by

$$\int_{\tau'} d\tau' \langle \vec{r} | D_\beta | \vec{r} \rangle \ ,$$

where

$$d\tau' \underline{\underline{\underline{\text{def}}}} \cdot \prod_{j=3}^{N} d^3\vec{r}_j, \quad \tau' \underline{\underline{\underline{\text{def}}}} \cdot V^{N-2} \ .$$

The quantum pair correlation function $g_\beta(n;\vec{r}_1,\vec{r}_2)$ is, then, defined by

$$g_\beta(n;\vec{r}_1,\vec{r}_2) \underline{\underline{\underline{\text{def}}}} \cdot \lim_{(V,N)\to\infty} V^2 \int_{\tau'} d\tau' \langle \vec{r} | D_\beta | \vec{r} \rangle \tag{131}$$

with

$$\lim_{(V,N)\to\infty} (N/V) = n \ (\text{finite}).$$

A further change in Eq. (131) can, by using the equation right above Eq. (99), be made in the following form:

$$g_\beta(n;\vec{r}_1,\vec{r}_2) \underline{\underline{\underline{\text{def}}}} \cdot \lim_{(V,N)\to\infty} V^2 e^{\beta F_\beta} \int_{\tau'} d\tau' \langle \vec{r}'s | S^\dagger e^{-\beta H} S | \vec{r}'s \rangle \tag{132}$$

where we note, in accordance with Eqs. (111) and (76), that

$$e^{-\beta F_\beta} \underline{\underline{\underline{\text{def}}}} \cdot \int_{V^2} d^3\vec{r}_1 d^3\vec{r}_2 \int_{\tau'} d\tau' \langle \vec{r}'s | S^\dagger e^{-\beta H} S | \vec{r}'s \rangle \ . \tag{133}$$

Equations (133) and (132) gives us a boundary condition of quantum pair

correlation function given by

$$\int_{\infty} d^3\vec{r}_1 d^3\vec{r}_2 g_\beta(n;\vec{r}_1,\vec{r}_2) = \underset{V\to\infty}{\ell im}\, V^2 \quad , \tag{134}$$

which is obtained also from Eq. (131) and (105).

Next, let us insert the identity operator given by Eq. (31) between two operators exp(-βH) and S in Eq. (132), and use Eq. (16). We have, then, a somewhat concrete form given by

$$g_\beta(n;\vec{r}_1,\vec{r}_2) = A_\beta \sum_{\vec{n}} e^{-\beta E_{\vec{n}}} \int_{\tau'} d\tau' \psi_{\vec{n}}(\vec{r})^* \psi_{\vec{n}}(\vec{r}), \tag{135}$$

where $\psi_{\vec{n}}(\vec{r})^*$ is the complex conjugate of the symmetrized energy-eigenfunction $\psi_{\vec{n}}(\vec{r})$ defined by

$$\psi_{\vec{n}}(\vec{r}) \overset{\text{def}}{\equiv} \cdot \langle \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N | S | \vec{n} \rangle / \equiv \langle \vec{r} | \vec{n} \rangle$$

with

$$H\psi_{\vec{n}}(\vec{r}) = E_{\vec{n}} \psi_{\vec{n}}(\vec{r}) \quad , \tag{136}$$

and A_β is an normalization operator defined by

$$A_\beta \overset{\text{def}}{\equiv} \cdot \underset{(V,N)\to\infty}{\ell im}\, V^2 e^{\beta F \beta} \quad .$$

The physical meaning of Eq. (135) is self-evident in connection with the law of large number of Eq. (48) and Eq. (24). Since the integral in Eq. (135) is a function of $\vec{r}_1$ and $\vec{r}_2$, we may write it also in the following form:

$$g_\beta(n;\vec{r}_1,\vec{r}_2) = A_\beta \sum_{\vec{n}} e^{-\beta E_{\vec{n}}} g_{\vec{n}}(N,V;\vec{r}_1,\vec{r}_2) \tag{137}$$

by defining

$$g_{\vec{n}}(N,V;\vec{r}_1,\vec{r}_2) \overset{\text{def}}{\equiv} \cdot \int_{\tau'} d\tau' \psi_{\vec{n}}(\vec{r})^* \psi_{\vec{n}}(\vec{r}) \quad , \tag{138}$$

which is temperature-independent. Equation (135), or Eq. (137) is the exact form of the quantum pair correlation function. This exact form will play a role of guidance in the determination of the approximate form of the quantum pair correlation function in a realistic problem.

We are now interested in deriving two specific forms of this pair correlation function at two specific absolute temperatures, i.e. $0^{o}K(\beta=\infty)$ and $\infty^{o}K(\beta=0)$ from Eq. (137). Let us change Eq. (137) into the following form:

$$g_{\beta} = A_{\beta} e^{-\beta E_{o}} [g_{\vec{o}} + \sum_{\vec{n}}{}' e^{-\beta(E_{\vec{n}}-E_{o})} g_{\vec{n}}], \tag{139}$$

where $\sum'$ represents the summation over all possible $\vec{n}$ except $\vec{n} = \vec{o}$ corresponding to the ground state of the system. We note, in Eq. (139), that

$$(E_{\vec{n}}-E_{o}) > 0, \quad g_{\vec{n}} = (\text{a bounded function independent of } \beta).$$

This character of boundness of $g_{\vec{n}}$ comes from the wave character of energy eigenfunction $\Psi_{\vec{n}}$. We have, thus in the limit of $\beta\to\infty$ in Eq. (139),

$$g_{\infty} = \lim_{\beta\to\infty} A_{\beta} e^{-\beta E_{o}} g_{\vec{o}}, \tag{140}$$

and then integrate Eq. (140) with respect to $\vec{r}_1$ and $\vec{r}_2$ over whole realistic space by noting Eq. (134) and the character of $g_{\vec{o}}$ normalizable to unity, to have

$$\lim_{(\beta,V,N)\to\infty} e^{\beta F_{\beta}} e^{-\beta E_{o}} = 1. \tag{141}$$

The combination of Eq. (141) with Eq. (140) gives us

$$g_{\infty}(n;\vec{r}_1,\vec{r}_2) = \lim_{V\to\infty} V^{2} \int_{\tau'} d\tau' \, \Psi_{o}(\vec{r})^{*} \Psi_{o}(\vec{r}), \tag{142}$$

by using the defintion given by Eq. (138). This is the relationship between the quantum pair correlation function g_∞ at absolute zero temperature and the ground state function $\psi_o(\vec{r})$ of the system. It should be pointed out from Eq. (142) that there is no contribution from any excited state to the quantum pair correlation function at absolute zero temperature, which implies physically that the system under consideration is exactly at its ground state at 0^oK. The exact determination of the function g_∞ depends upon finding the exact energy eigenfunction of ground state by solving directly, or indirectly Eq. (136).

At extremely high temperature $\beta \to 0$, we have, by using Eq. (137),

$$g_o = \lim_{V\to\infty} V^2 \sum_{\vec{n}} g_{\vec{n}} = \lim_{V\to\infty} V^2 \sum_{\vec{n}} \int_{\tau'} d\tau' \psi_{\vec{n}} \psi^*_{\vec{n}}, \tag{143}$$

which shows us that the system is likely equally at any possible excited state including its ground state at ∞^oK. As shown in Eq. (143), we need to find all the energy eigenfunctions in order to determine the exact form of the quantum pair correlation function g_o at ∞^oK in contrast to the case of g_∞ .

As shown in Eqs. (143), (142), and (135), it is quite obvious that the quantum pair correlation function has, in general, an oscillatory character due to the wave character of the energy eigenfunction of the system. Since we have, from Eq. (134),

$$\int_\infty d^3\vec{r}_1 d^3\vec{r}_2 (g_\beta - 1) = 0; \tag{144}$$

this oscillatory character must occur around the value 1, and its

feature depends upon the type of interaction between particles in the system. In the realistic problem, this interaction is varying very slowly with the increase of $|\vec{r}_2-\vec{r}_1|$ for $|\vec{r}_2-\vec{r}_1|$ large enough. This causes the slowly varying feature of $|\psi_{\vec{n}}(\vec{r})|^2$, or $g_{\vec{n}}$ defined by Eq. (138) for $|\vec{r}_2-\vec{r}_1|$ large enough, so that we may have, from Eq. (138),

$$\lim_{|\vec{r}_2-\vec{r}_1|\to\infty}\lim_{V\to\infty} g_{\vec{n}} = \lim_{|\vec{r}_2-\vec{r}_1|\to\infty}\lim_{V\to\infty} V^2\int_{\tau'}|\psi_{\vec{n}}|^2 d\tau'$$

$$= \int_{\infty} d^{3N}\vec{r}\,|\psi_{\vec{n}}|^2 = 1 \tag{145}$$

by noting the normalization condition of $\psi_{\vec{n}}(\vec{r})$. Now, we combine Eq. (145) with Eq. (137) by replacing the operator A_β by its original one, to see that

$$\lim_{|\vec{r}_2-\vec{r}_1|\to\infty} g_\beta(n;\vec{r}_1,\vec{r}_2) = 1 \tag{146}$$

by using also Eq. (49) and the second of Eq. (50).

Equation (132) defining the quantum pair correlation function may be written also as

$$g_\beta(n;\vec{r}_1,\vec{r}_2) = A_\beta\int_{\tau'} d\tau' \langle \vec{r}'s|Se^{-\beta H}|\vec{r}'s\rangle \tag{147}$$

by using the normalization operator A_β, Eqs. (96) and (76), and also

$$g_\beta^{\pm}(n;\vec{r}_1,\vec{r}_2) = \frac{A_\beta}{N!}\sum_{\Pi}(\pm)^{\Pi}\int_{\tau'} d\tau' \langle \vec{r}'s|\Pi e^{-\beta H}|\vec{r}'s\rangle \tag{148}$$

by substituting Eq. (72) into Eq. (147). We may, in analogy with Eq. (115), expand Eq. (148) in the following form.

$$g_{\beta}^{\pm}(n;\vec{r}_1,\vec{r}_2) = \frac{A_\beta}{N!}\int_{\tau'} d\tau' \langle \vec{r}'s \,|\, e^{-\beta H} |\vec{r}'s\rangle + \sum_{i=2}^{C(N)} (\pm)^{p_i} \boxed{\sum_{\lambda=1}^{m_i} \Gamma_i^{\lambda}(\beta,n;\vec{r}_1,\vec{r}_2)} \tag{149}$$

with

$$\Gamma_i^{\lambda}(\beta,n;\vec{r}_1,\vec{r}_2) \overset{\text{def.}}{\equiv} \frac{A_\beta}{N!}\int_{\tau'} d\tau' \langle \vec{r}'s \,|\, \Pi_i^{\lambda} e^{-\beta H} |\vec{r}'s\rangle \ . \tag{150}$$

This is the symmetric group class expansion formula for the quantum pair correlation function. This expansion has a different feature from that of the quantum partition function Q_β of canonical ensemble. All of the element functions Γ_i^{λ} (λ=1,2,...,m_i) in the same class (the ith class C_i) are not the same. They have their own structure, and some of them are equivalent to each other. We call this the fine structure of the same class element. This feature is due to the volume element given by $d\tau' \equiv \prod_{j=3}^{N} d^3\vec{r}_j$ instead of $d^{3N}\vec{r}$. However, there is always a number of the different fine structures less than the total number m_i of the elements in a class C_i. In another word, we can find always the same integrals defined by Eq. (150) in a class. This fact is formally very much similar to the diagram expansion theory for the classical radial distribution function.[25] It may be possible that we develop a new formal expansion theory of the quantum pair correlation function in analogy with the idea of the classical expansion theory. In Eq. (149), the first integral is the first class term corresponding to the identity element, which gives us no distinguishability between the boson and fermion systems, even though it makes the quantum effects but no exchange

effects of the system under consideration. We call, therefore, the function $g_\beta^{(1)}$ defined by

$$g_\beta^{(1)}(n;\vec{r}_1,\vec{r}_2) \overset{\text{def.}}{=\!=} \frac{A_\beta}{N!}\int_{\tau'} d\tau' \langle \vec{r}'s | e^{-\beta H} | \vec{r}'s \rangle \tag{151}$$

the quasi-quantum pair correlation function of the system in question in analogy with the nomenclature in the case of the quasi-quantum partition function defined by Eq. (108). Eq. (151) corresponds to the corrected Maxwell-Boltzmann's statistics. The second part of double summation represents the exchange effects of identical, indistinguishable particles in addition to the quantum effects. According to Landau and Lifshitz, these exchange effects are small at high temperature but very significant at very low temperature.[26] We can develop also the approximation theory of our quantum pair correlation function in analogy with that of the quantum partition function of canonical ensemble developed in the previous section.

Let us change Eq. (151) into the form convenient for a concrete calculation by using the identity operator constructed from the eigenkets of wave vector operator. It gives, then, us

$$g_\beta^{(1)}(n;\vec{r}_1,\vec{r}_2) = \frac{A_\beta}{N!}(1/2\pi)^{3N}\int_{\tau'} d\tau' \int_\infty d^{3N}\vec{k}\, \boxed{e^{-i\vec{k}\cdot\vec{r}_e - \beta H_e i\vec{k}\cdot\vec{r}}} \tag{152}$$

We see here again the same function $F'_\beta(\vec{k},\vec{r})$ defined by Eq. (126) inside the dot rectangle as that encountered in the previous section.

We will, in Chapter III, study the concrete determination of the quantum pair correlation function defined by Eq. (152) and the function $F'_\beta(\vec{k},\vec{r})$ by using the W.K.B. approximation method.

CHAPTER III

THE W.K.B. APPROXIMATION FOR THE QUANTUM RADIAL DISTRIBUTION FUNCTION

—For those well ordered motions, and regular paces, though they give no sound unto the ear, yet to the understanding they strike a note most full of harmony—(Sir Thomas Browne)

3.1. The Concrete Determination of the Function $F'_\beta(\vec{k},\vec{r})$

We rewrite, here again, the definition of the function $F'_\beta(\vec{k},\vec{r})$ given by Eq. (126):

$$F'_\beta(\vec{k},\vec{r}) = e^{-i\vec{k}\cdot\vec{r}} e^{-\beta H} e^{i\vec{k}\cdot\vec{r}} \quad . \tag{153}$$

This function can be constructed also from the diagonal element $D'_\beta(\vec{r},\vec{r})$ of the so-called quasi-Neumann's density matrix $D'_\beta(\vec{r},\vec{r}')$(disregarding the particle exchange effects) defined by

$$D'_\beta(\vec{r},\vec{r}') \stackrel{\text{def.}}{\equiv} e^{\beta F_\beta} \langle \vec{r}'s | e^{-\beta H} | \vec{r}''s \rangle \quad . \tag{154}$$

by inserting the identity operator I given by Eq. (100)' between the operator exp(-βH) and the ket vector $|\vec{r}''s\rangle$ in Eq. (154), where $|\vec{r}'s\rangle$ is defined by the expression immediately subsequent to Eq. (100). Historically, the use of this identity operator I was introduced firstly by Kirkwood in developing his expansion theory of the so-called quasi-Slater sum.[27] Uhlenbeck and Beth have repeated the Kirkwood's expansion calculation and extended it in their paper,[28] and later they have used it for calculating the quantum virial coefficient at low temperature.[29]

Furthermore, de Boer has taken also their expansion expression in developing his theory of the equation of state by introducing the so-called de Boer factor ($\Lambda \equiv \hbar/a\sqrt{mc}$).[30,31] On the other hand, the approach of finding the Slater sum by solving the Bloch equation has been done by Husimi, Mayer, and Band.[32,33] Recently, ter Haar, Landau and Lipshitz have, in an elegant way, developed this expansion theory in their books.[26,34] All of these expansion theories have been constructed so that they are rather powerful for the theory of the equation of state of quasi-quantum fluid over some low temperature.

However, we are, now in this dissertation, concerned with a somewhat different expansion theory of the function $F'_{\beta}(\vec{k},\vec{r})$ defined by Eq. (153) from those done by our predecessors. Our expansion theory to be developed hereafter must be rather useful for the theory of quantum pair correlation function $g_{\beta}(n;\vec{r}_1,\vec{r}_2)$ than for the theory of the equation of state. Furthermore, it should be made within that it can be led finally to the formal classical case with an effective potential varying also with the temperature. This requirement comes from the Broyles' program[18] that the Percus-Yevick, or the Convolution Hyper-Netted chain nonlinear integral equation of the classical radial distribution function can be applied to the numerical determination of the function $g_{\beta}(n;\vec{r}_1,\vec{r}_2)$ by using the computing machine. We will discuss about these two nonlinear integral equations in next section.

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[18]This program is suggested first by Dr. A. A. Broyles, Professor of Physics, University of Florida, Gainesville, Florida, U.S.A. To the author's best knowledge of this paper, this program is the most powerful method in the theory of fluid, at least at present, compared with the several methods suggested by other authors.

Now, let us, in terms of the function $F'_\beta(\vec{k},\vec{r})$ defined by Eq. (153), write the diagonal element of the exact Neumann's density matrix given by Eq. (101) in the following form:

$$D^{\pm}_\beta(\vec{r},\vec{r}) = \frac{\exp(\beta F^{\pm}_\beta)}{(2\pi)^{3N}N!}\sum_{\Pi}(\pm 1)^{\Pi}\int_{\infty} d^{3N}\vec{k}\, e^{i\vec{k}\cdot(\vec{r}-\Pi\vec{r})}F'_\beta(\vec{k},\vec{r}), \tag{155}$$

and at first consider the case of an ideal fluid. Our function $F'_\beta(\vec{k},\vec{r})$ becomes, in this case, simply

$$F'_\beta(\vec{k},\vec{r}) = e^{-\beta\hbar^2\vec{k}^2/2m}, \tag{156}$$

and therefore Eq. (155) takes the following explicit form:

$$D^{\pm}_\beta(\vec{r},\vec{r}) = \frac{\exp(\beta F^{\pm}_\beta)}{N!\,\lambda^{3N}}\sum_{\Pi}(\pm 1)^{\Pi}e^{-\pi(\vec{r}-\Pi\vec{r})^2/\lambda^2}, \tag{157}$$

[19]

$$(\lambda \overset{\text{def.}}{=\!=} \hbar(2\pi\beta/m)^{\frac{1}{2}}),$$

where m is the mass of a particle of the ideal fluid under consideration, and λ, its thermal de Broglie's wave length. This result shows us that there is the apparent attraction between Bose-Einstein particles, while the apparent repulsion between Fermi-Dirac particles.

It seems that the function $F'_\beta(\vec{k},\vec{r})$ may not, in general, be expressed explicitly by an elementary function in the case of realistic imperfect fluid except that of the simple imperfect fluid. We will quote below the three results of $D_\beta(\vec{r},\vec{r})$ obtained in the three simple systems respectively.

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[19] We have used here the formula given by

$$\int_{-\infty}^{\infty} dx\, \exp(-a^2x^2+ibx) = \pi^{\frac{1}{2}}a^{-1}\exp(-b^2/4a^2). \quad \text{(AIII)}$$

(i) A system of one particle enclosed in a 1-dimensional box with a finite size:

$$D_\beta(x,x) = \frac{\exp(\beta F_\beta)}{\lambda}\left(1-e^{-4\pi x^2/\lambda^2}\right)$$

(ii) A system of a linear harmonic oscillator with an angular frequency ω:

$$D_\beta(x,x) = \frac{\exp(\beta F_\beta)}{\lambda}\left[\frac{2\pi\hbar\beta}{1-\exp(2\pi\hbar\beta)}\right]^{\frac{1}{2}} \exp\left(-\frac{\pi\hbar\beta}{2}\frac{m\omega}{\pi\hbar}\, x^2 \tanh\frac{\pi\hbar\beta}{2}\right)$$

(iii) A system of two identical, indistinguishable particles enclosed in a 1-dimensional box with a finite size:

$$D_\beta^{\pm}(\vec{x},\vec{x}) = \frac{\exp(\beta F_\beta^{\pm})}{2!\,\lambda^2}\left[\left(1-e^{-4\pi x_1^2/\lambda^2}\right)\left(1-e^{-4\pi x_2^2/\lambda^2}\right) \pm \left(e^{-\pi(x_1-x_2)^2/\lambda^2} - e^{-\pi(x_1+x_2)^2/\lambda^2}\right)\right] . \quad (17,35)^{20}$$

Incidentally, it is valuable to note that the Neumann's density matrix $D_\beta(\vec{r},\vec{r}')$ can be found also by solving a differential equation with a boundary condition, instead of calculating the integral given by Eq. (155). We will show the correctness of this statement as follows: Let us consider the function $X_\beta(\vec{r},\vec{r}')$ defined by

$$X_\beta(\vec{r},\vec{r}') \overset{\text{def}}{=\!=} e^{-\beta F_\beta} D_\beta(\vec{r},\vec{r}') = \langle \vec{r}|e^{-\beta H}|\vec{r}'\rangle , \quad (158)$$

or

$$D_\beta(\vec{r},\vec{r}') = e^{\beta F_\beta} X_\beta(\vec{r},\vec{r}'). \quad (158)'$$

This function $X_\beta(\vec{r},\vec{r}')$ with $\vec{r}'=\vec{r}$ is equivalent to the Slater sum with

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[20] In these 3 systems, $\exp(\beta F_\beta)$ can be easily found by the normalization condition of D_β and the calculation of the Gauss' probability integral.

the difference of the factorial coefficient N! (see Eq. (55)). The differentiation of Eq. (158) with respect to the parameter β gives us the following result:

$$\partial_\beta X_\beta(\vec{r},\vec{r}') = -\langle\vec{r}|He^{-\beta H}|\vec{r}'\rangle$$

or

$$\partial_\beta X_\beta = -HX_\beta \qquad (159)$$

by taking out the Hamiltonian operator H before the bra vector $\langle\vec{r}|$ and changing it into its equivalent differential operator $H(-i\hbar\vec{\partial},\vec{r})$ in the $\vec{r}$-representation. Eq. (159) is the Bloch equation. The Bloch equation is, thus, satisfied also by the function $X_\beta(\vec{r},\vec{r}')$ as well as the Bloch function $U_\beta(\vec{k},\vec{r})$ defined by Eq. (62). But their boundary condition for temperature are different from each other. The temperature-boundary condition for the function $X_\beta(\vec{r},\vec{r}')$ can be found immediately from Eq. (158), i.e.

$$\lim_{\beta\to 0} X_\beta(\vec{r},\vec{r}') = \langle\vec{r}|\vec{r}'\rangle \equiv \langle\vec{r}'s|s|\vec{r}'s\rangle, \qquad (160)$$

where the function $\langle\vec{r}|\vec{r}'\rangle$ is defined by Eq. (90). The variable $\vec{r}'$ goes in the solution of Eq. (159) as a parameter through this boundary condition.

Now, we are going to have a change in the function $F'_\beta(\vec{k},\vec{r})$ defined by Eq. (153). Before doing this, we introduce the total kinetic energy operator T and potential energy operator Φ of the system

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[21] It is noticeable that this equation is formally equivalent to the Schrödinger's time-dependent equation.

under consideration, and assume that the operator Φ does not depend upon the particle-momentum operator, i.e.

$$T \overset{\text{def.}}{=\!=} -\frac{\hbar^2}{2m}\vec{\partial}^2, \quad \Phi \overset{\text{def.}}{=\!=} \Phi(\vec{r}). \tag{161}$$

The Hamiltonian operator H of the system is, then, written as

$$H = -\alpha\vec{\partial}^2 + \Phi(\vec{r}) = T + \Phi \tag{162}$$

by defining a microscopic-characteristic constant α of the particle of the system given by

$$\alpha \overset{\text{def.}}{=\!=} \hbar^2/2m\,, \tag{163}$$

and Eq. (153) takes the following form:

$$F'_\beta(\vec{k},\vec{r}) = e^{-i\vec{k}\cdot\vec{r}} e^{-\beta\Phi-\beta T} e^{i\vec{k}\cdot\vec{r}}\,. \tag{164}$$

We insert, next, the identity operator $\exp(\beta T)\exp(-\beta T)$ between the operator $\exp(-\beta\Phi-\beta T)$ and the operand $\exp(i\vec{k}\cdot\vec{r})$, to have

$$F'_\beta(\vec{k},\vec{r}) = e^{-i\vec{k}\cdot\vec{r}} e^{-\beta\Phi-\beta T}\, e^{\beta T}\left(e^{-\beta T} e^{i\vec{k}\cdot\vec{r}}\right)$$

or

$$F'_\beta(\vec{k},\vec{r}) = e^{-\beta H_c}\, f_\beta(\alpha;\vec{k},\vec{r}) \tag{165}$$

by noting that the part of the parenthesis ( ) becomes

$$e^{-\beta T} e^{i\vec{k}\cdot\vec{r}} = e^{-\alpha\beta\vec{k}^2} e^{i\vec{k}\cdot\vec{r}}$$

with a c-number $\exp(-\alpha\beta\vec{k}^2)$, and defining the classical Hamiltonian H_c, an operator Ω_β, and a function $f_\beta(\alpha;\vec{k},\vec{r})$ given by

$$H_c \overset{\text{def}}{\equiv} \cdot \alpha \vec{k}^2 + \Phi(\vec{r}),$$

$$\mathcal{\Omega}_\beta \overset{\text{def}}{\equiv} \cdot e^{\beta\Phi} e^{-\beta(\Phi+T)} e^{\beta T}, \tag{166}$$

$$f_\beta(\alpha;\vec{k},\vec{r}) \overset{\text{def}}{\equiv} \cdot e^{-i\vec{k}\cdot\vec{r}} \mathcal{\Omega}_\beta e^{i\vec{k}\cdot\vec{r}}$$

As shown in Eq. (165), the explicit determination of the function $F'_\beta(\vec{k},\vec{r})$ is dependent upon finding the explicit form of the function $f_\beta(\alpha;\vec{k},\vec{r})$ defined by the last of Eq. (166). It is believed that there are two ways to find the function $f_\beta(\alpha;\vec{k},\vec{r})$ in this kind of formalism. The one way is to change the operator $\mathcal{\Omega}_\beta$ into such a form that it can operate out on the operand $\exp(i\vec{k}\cdot\vec{r})$. The other way is to find the function $f_\beta(\alpha;\vec{k},\vec{r})$ directly by solving a differential equation satisfied by it. According to the author's study of this paper, as we will show immediately, the former method is suitable for very high temperature region, and the latter is believed to be powerful for the region up to the fairly low temperature. However, it seems that our method to be presented hereafter in this dissertation would fail in the region of extremely low temperature.

A. The First Method Effective for Very High Temperature:

We expand the operator $\mathcal{\Omega}_\beta$ given by the second of Eq. (166) in the ascending power series of β as follows:

$$\mathcal{\Omega}_\beta \equiv e^{\beta\Phi} e^{-\beta(\Phi+T)} e^{\beta T} = \sum_{(\lambda,\mu,\nu)=(0,0,0)}^{\infty} (-1)^{\mu} \beta^{\lambda+\mu+\nu} \frac{\Phi^\lambda (\Phi+T)^\mu T^\nu}{\lambda!\,\mu!\,\nu!}$$

or

$$\mathcal{\Omega}_\beta = \sum_{(\lambda+\mu+\nu=n)}^{\infty} \beta^n \mathcal{\Omega}_\beta^{(n)} \quad , \tag{167}$$

by defining

$$\mathcal{A}_{\beta}^{(n)} \underset{\text{def.}}{=} \sum_{\substack{(\lambda,\mu,\nu) \\ (\lambda+\mu+\nu=n)}} (-1)^{\mu_{\beta}n} \frac{\phi^{\lambda}(\phi+T)^{\mu}T^{\nu}}{\lambda!\mu!\nu!} , \tag{168}$$

where the summation goes over all 3-dimensional lattice points (λ,μ,ν) satisfying the condition given by

$$\begin{aligned} &\lambda+\mu+\nu = n; \quad n = 0,1,2,3,\ldots; \\ &\lambda \geq 0, \ \mu \geq 0, \ \nu \geq 0 \quad . \end{aligned} \tag{169}$$

The number $f(n)$ of the lattice points (λ,μ,ν) satisfying the condition of Eq. (169) for a given positive integer n is seen easily to be given by

$$f(n) = {}_{n+3-1}C_{3-1} = {}_{n+2}C_{2} = \frac{(n+2)(n+1)}{2!} , \tag{170}$$

[22]

by observing the same countings as that of Bose-Einstein statistics. We will calculate the first four terms of Eq. (167), i.e. the terms corresponding to n = 0,1,2,3, below, respectively.

The first term: The number $f(0)$ of the lattice point (λ,μ,ν) satisfying the condition $\lambda+\mu+\nu = 0$ is, from Eq. (170),

$$f(0) = 1,$$

and it is $(\lambda,\mu,\nu) = (0,0,0)$. We have therefore from Eq. (168),

$$\mathcal{A}_{\beta}^{(0)} = I \text{ (identity)} \tag{171}$$

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[22] The notation, e.g. nCm represents the total number of combination ways choosing m things among n things ($n \geq m$).

The second term: The number $f(1)$ under the condition $\lambda+\mu+\nu = 1$ is, from Eq. (170),

$$f(1) = 3,$$

and the 3 lattice points are

$$(\lambda,\mu,\nu) = (1,0,0);\ (0,1,0);\ (0,0,1).$$

Hence, we have, from Eq. (168),

$$\mathcal{A}_{\beta}^{(1)} = \frac{\Phi}{1!0!0!} - \frac{\Phi + T}{0!1!0!} + \frac{T}{0!0!1!} = 0. \tag{172}$$

The third term: The number $f(2)$ under the condition $\lambda+\mu+\nu = 2$ is $f(2) = 6$, and the 6 lattice points are given by

$$(\lambda.\mu.\nu) = \begin{matrix}(2,0,0);\ (1,1,0);\ (0,2,0);\\ (1,0,1);\ (0,0,2);\ (0,1,1).\end{matrix}$$

We have, thus from Eq. (168),

$$\mathcal{A}_{\beta}^{(2)} = \frac{\Phi^2}{2!} + \frac{(\Phi+T)^2}{2!} + \frac{T^2}{2!} - \frac{\Phi(\Phi+T)}{1!1!} + \frac{\Phi T}{1!1!} - \frac{(\Phi+T)T}{1!1!},$$

or

$$\mathcal{A}_{\beta}^{(2)} = \frac{1}{2!}[T,\Phi] = -\frac{\alpha}{2!}[(\vec{\partial}^2\Phi) + 2(\vec{\partial}\Phi)\cdot\vec{\partial}] \tag{173}$$

The fourth term: The number $f(3)$ is given by $f(3) = {}_5C_2 = 10$, and the calculated result of the operator $\mathcal{A}_{\beta}^{(3)}$ is as follows:

$$\mathcal{A}_{\beta}^{(3)} = \frac{1}{3!}[(T-\Phi),[T,\Phi]]$$

$$= -\frac{\alpha}{3!}[(\alpha\vec{\partial}^2\Phi)\{(\vec{\partial}^2\Phi) + 2(\vec{\partial}\Phi)\cdot\vec{\partial}\}]$$

$$= \frac{\alpha}{3!}[2(\vec{\partial}\Phi)^2 - \alpha\{(\vec{\partial}^4\Phi) + 4(\vec{\partial}^2\vec{\partial}\Phi)\cdot\vec{\partial} + 4(\vec{\partial}\vec{\partial}\Phi):\vec{\partial}\vec{\partial}\}].^{23} \tag{174}$$

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[23] The double dot ":" represents the scalar double dot product of two dyadics. e.g. see P. M. Morse and H. Feshbach; Methods of Theoretical Physics, Vol. 1, p54 et seq., (1954).

The number $f(4)$ of the lattice points for the fifth term is $f(4) = {}_6C_2 = 15$, and for the sixth term, $f(5) = {}_7C_2 = 21$, and so on.

We have, thus on substituting Eqs. (174), 173), (172), and (171) into Eq. (167),

$$\mathcal{\Omega}_\beta = I - \frac{\alpha\beta^2}{2!}[(\vec{\partial}^2\phi) + 2(\vec{\partial}\phi)\cdot\vec{\partial}] + \frac{\alpha\beta^3}{3!}[2(\vec{\partial}\phi)^2$$

$$- \alpha\{(\vec{\partial}^4\phi) + 4(\vec{\partial}^2\vec{\partial}\phi)\cdot\vec{\partial} + 4(\vec{\partial}\vec{\partial}\phi):\vec{\partial}\vec{\partial}]] + \ldots \qquad (175)$$

The substitution of this expansion of the operator $\mathcal{\Omega}_\beta$ into the last of Eq. (166) gives us the following result:

$$f_\beta(\alpha;\vec{k},\vec{r}) = 1 - \frac{\alpha\beta^2}{2!}[(\vec{\partial}^2\phi) + 2i\vec{k}\cdot\vec{\partial}\phi] + \frac{\alpha\beta^3}{3!}[2(\vec{\partial}\phi)^2$$

$$- \alpha\{(\vec{\partial}^4\phi) + 4i\vec{k}\cdot\vec{\partial}\vec{\partial}^2\phi - 4\vec{k}\cdot\vec{\partial}\vec{\partial}\phi\cdot\vec{k}]\} + \ldots . \qquad (176)$$

This result allows us to find the function $F'_\beta(\vec{k},\vec{r})$ in the power series form of β by combining Eqs. (176) and (165). This is the case only at the point $(\vec{r},\vec{k})$ in phase space where the power series of β given by Eq. (176) is convergent under the assumption that the given potential $\phi(\vec{r})$ is an analytic function at the point $\vec{r}$ in configuration space. It is evident, from the power series form of Eq. (176), that this expansion result is useful only for the region of very high temperature.

B. The Second Method Effective for the Region up to the Fairly Low Temperature:

Before we construct the differential equation satisfied by the function $f_\beta(\alpha;\vec{k},\vec{r})$, we investigate, at first, the several properties of this function for the sake of the familiarity with it, and also for the

reference of our later discussions. We will describe briefly the proofs needed for us in our discussions.

Property 3.1: The dimensionless function $f_\beta(\vec{k},\vec{r})$ is neither a real function nor a pure imaginary function. It is really a complex function having the formal form given by

$$f_\beta = f_\beta^{(r)} + i f_\beta^{(i)}, \quad (i \equiv \sqrt{-1}),$$

with (176)'

$$f_\beta^{(r)} \equiv \cos \vec{k}\cdot\vec{r}\,\mathcal{A}_\beta \cos \vec{k}\cdot\vec{r} + \sin \vec{k}\cdot\vec{r}\,\mathcal{A}_\beta \sin \vec{k}\cdot\vec{r},$$

$$f_\beta^{(i)} \equiv \cos \vec{k}\cdot\vec{r}\,\mathcal{A}_\beta \sin \vec{k}\cdot\vec{r} - \sin \vec{k}\cdot\vec{r}\,\mathcal{A}_\beta \cos \vec{k}\cdot\vec{r} .$$

Proof: The formal forms of $f_\beta^{(r)}$ and $f_\beta^{(i)}$ are resulted from the use of Euler's theorem given by

$$e^{\pm i\vec{k}\cdot\vec{r}} = \cos \vec{k}\cdot\vec{r} \pm i \sin \vec{k}\cdot\vec{r} ,$$

and it is obvious, from Eq. (176), that $f_\beta^{(r)} f_\beta^{(i)} \neq 0$ at every point $(\vec{r},\vec{k})$ in the phase space.

Property 3.2: The function f_β contains both of the independent variables $\vec{r}$ and $\vec{k}$ within it, i.e. we must write

$$f_\beta = f_\beta(\vec{k},\vec{r}) .$$

Proof: The dependence on $\vec{k}$ is self-evident in accordance with the form of the operator $\mathcal{A}_\beta$. Actually, it is proved as follows: Let us apply the gradient operator $\vec{\partial}$ in $\vec{k}$-space on the function f_β. We have, then after a simple calculation,

$$\vec{\partial} f_\beta = i e^{-i\vec{k}\cdot\vec{r}} [\mathcal{A}_\beta, \vec{r}] e^{i\vec{k}\cdot\vec{r}} ,$$

or $$\vec{\partial} f_\beta \neq 0,$$

since we have, always, $[\mathcal{L}_\beta, \vec{r}] \neq 0$, $(\beta \neq 0)$. This shows us that f_β contains, at least, the variable $\vec{k}$ in it. Similarly, we can show that

$$\vec{\partial} f_\beta \neq 0.$$

Property 3.3: The boundary value $f_\beta(\vec{k},\vec{r})$ at $\beta = 0$ $(T=\infty)$ is unity at every point $(\vec{k},\vec{r})$ in the phase space, i.e.

$$[f_\beta(\vec{k},\vec{r})]_{\beta=0} = 1 \ . \tag{177}$$

Proof: This is obvious, from the boundary condition of the function $F'_\beta(\vec{k},\vec{r})$ given by Eq. (127) and Eq. (165). Or, we can see this property from the second and the third of Eq. (166) by noting $(\mathcal{L}_\beta)_{\beta=0} = I$.

Property 3.4: The function $f_\beta(\vec{k},\vec{r})$ is completely symmetric for the inversion, reflection (within its complex conjugate), and exchange operations in phase space, i.e.

$$\begin{aligned} f_\beta(-\vec{k},-\vec{r}) &= f_\beta(\vec{k},\vec{r}) \ , \\ f_\beta(-\vec{k},\vec{r}) &= f_\beta(\vec{k},-\vec{r}) = f^*_\beta(\vec{k},\vec{r}), \\ \Pi_{\lambda\mu} f_\beta(\vec{k},\vec{r}) &= f_\beta(\vec{k},\vec{r}) \ , \end{aligned} \tag{178}$$

where $\Pi_{\lambda\mu}$ is the exchange operator exchanging two particles at the two points $(\vec{r}_\lambda,\vec{k}_\lambda)$ and $(\vec{r}_\mu,\vec{k}_\mu)$ in the phase space, and the symbol "$*$" represents complex conjugate.

Proof: This property is quite clear, from the definition of the function $f_\beta(\vec{k},\vec{r})$ given by Eq. (166), on the basis of the fact that $\vec{k}\cdot\vec{r}$ = (invariant), T = (invariant), and $\Phi(\vec{r})$ = (invariant due to the isotropic property of the realistic space) under these operations.

Property 3.5: The function $f_\beta(\vec{k},\vec{r})$ is related to the Bloch function $U_\beta(\vec{k},\vec{r})$ by

$$U_\beta(\vec{k},\vec{r}) = e^{-(\beta H_c - i\vec{k}\cdot\vec{r})} f_\beta(\vec{k},\vec{r}). \tag{179}$$

Proof: We have from Eqs. (165) and (153),

$$e^{-i\vec{k}\cdot\vec{r}}\boxed{e^{-\beta H} e^{i\vec{k}\cdot\vec{r}}} = e^{-\beta H_c} f_\beta(\vec{k},\vec{r}) \quad .$$

This leads to Eq. (179) with the use of the definition of the Bloch function given by

$$U_\beta(\vec{k},\vec{r}) \overset{\text{def}}{\equiv} e^{-\beta H} e^{i\vec{k}\cdot\vec{r}} \quad [24] \tag{180}$$

which satisfies the Bloch equation:

$$(\partial_\beta + H) U_\beta = 0. \tag{181}$$

We finish our brief description about the property of the function f_β with this. Next, we construct a differential equation satisfied by the function f_β, which makes the most important basis of our subsequent theory.

Let us differentiate the last of Eq. (166) with respect to the parameter β referring to the second of Eq. (166). We have, then,

$$\begin{aligned} \partial_\beta f_\beta &= e^{-i\vec{k}\cdot\vec{r}} (\partial_\beta \Omega_\beta) e^{i\vec{k}\cdot\vec{r}} \\ &= e^{-i\vec{k}\cdot\vec{r}} \Omega_\beta T e^{i\vec{k}\cdot\vec{r}} - (e^{-i\vec{k}\cdot\vec{r}} e^{\beta\Phi} T e^{-\beta\Phi} e^{i\vec{k}\cdot\vec{r}})(e^{-i\vec{k}\cdot\vec{r}} \Omega_\beta e^{i\vec{k}\cdot\vec{r}}) \end{aligned}$$

or

$$\partial_\beta f_\beta = \overrightarrow{\alpha k}^2 f_\beta - \boxed{e^{\beta\Phi - i\vec{k}\cdot\vec{r}} T e^{-(\beta\Phi - i\vec{k}\cdot\vec{r})}} f_\beta, \tag{182}$$

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[24] Exactly speaking, this function may be called the quasi-Bloch function (disregarding the particle exchange effects) in contrast with the definition of Eq. (62).

by operating out the operator T on its operand in the first term of the right-hand side. The operator inside of [------] in Eq. (182) is the similar transformation of the kinetic energy operator T of the system by an operator $\exp(\beta\Phi - i\vec{k}\cdot\vec{r})$. We change the differential equation of second order given by Eq. (182) into a more accessible one. We operate out the operator T on its operand $\exp(-\beta\Phi + i\vec{k}\cdot\vec{r})$ in the right hand side of Eq. (182). We have, then after some calculations,

$$\partial_\beta f_\beta = \left[\alpha\vec{\partial}^2 - 2\alpha\beta\vec{\partial}\Phi\cdot\vec{\partial} - \alpha\beta(\vec{\partial}^2\Phi) + \alpha\beta^2(\vec{\partial}\Phi\cdot\vec{\partial}\Phi) - 2i\alpha\vec{k}\cdot\{\beta(\vec{\partial}\Phi) - \vec{\partial}\}\right] f_\beta \quad . \tag{183}$$

[25]

We note here that the operator inside of [ ] in the right-hand side of Eq. (183) is a linear operator. Therefore, Eq. (183) is a linear partial differential equation of second order, and the solution to this equation must satisfy the boundary condition given by Eq. (177). The last complex term of Eq. (183) given by

$$2i\alpha\vec{k}\cdot\{\beta f_\beta\vec{\partial}\Phi - \vec{\partial} f_\beta\} \tag{184}$$

in an unfortunate term in finding the function f_β. We can not see the general reason to neglect this unlucky term. Nevertheless, it is desirable to exclude this unlucky term for the sake of our more accessible treatment of Eq. (183). However, we will show below the fact that we are led to a very dangerous result if we neglect this unhappy term.

The neglection of this unlucky term corresponds to regarding

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[25] This is, in fact, an alternative form of the Bloch equation, since Eq. (183) can be derivable from the Bloch equation of Eq. (181) by substituting Eq. (179) into it, and vice versa.

the function f_β possibly as a real function, and makes Eq. (183) be written as

$$\partial_\beta f_\beta = \alpha\vec{\partial}^2 f_\beta - 2\alpha\beta\vec{\partial}\Phi\cdot\vec{\partial}f_\beta + \alpha\beta[\beta(\vec{\partial}\Phi\cdot\vec{\partial}\Phi)-(\vec{\partial}^2\Phi)]f_\beta \ .$$

This equation can be reduced to the following form:

$$\partial_\beta f_\beta = - e^{\beta\Phi}T\, e^{-\beta\Phi} f_\beta \ , \tag{185}$$

which is obtainable also by putting $\vec{k} = 0$ in Eq. (182). Since Eq. (185) does not contain the variable $\vec{k}$, the function f_β takes the form given by

$$f_\beta = f_\beta(\alpha;\vec{r}) \ .$$

This result obtained by neglecting Eq. (184) implies physically that the contribution of the particle-momenta ($=\hbar\vec{k}$) to the function f_β comes mainly from the zero momenta ($\vec{k}=0$), i.e. the particles at rest. However, this is not physically the case. Now, Eq. (185) can be, after a simple arrangement, changed into the form of the Bloch equation given by

$$(T+\Phi)v_\beta = -\partial_\beta v_\beta, \quad \text{or} \quad \partial_\beta v_\beta = Hv_\beta \tag{186}$$

by putting

$$v_\beta = e^{-\beta\Phi(\vec{r})} f_\beta(\alpha;\vec{r}) \ . \tag{187}$$

Noting that Eq. (186) is a linear equation, we may assume the solution to it in the following form:

$$v_\beta = e^{-\beta E_{\vec{n}}} v_{\vec{n}}(\vec{r}) \tag{188}$$

with a constant $E_{\vec{n}}$. We have, then on substituting Eq. (188) into Eq. (186),

$$H\Psi_{\vec{n}}(\vec{r}) = E_{\vec{n}}\Psi_{\vec{n}}(\vec{r}) \quad .$$

This is the familiar time-independent Schrödinger's equation of the system under consideration. Therefore, the function $\Psi_{\vec{n}}(\vec{r})$ contained in a solution of Eq. (188) to the Bloch equation of Eq. (186) is really equal to the eigenfunction corresponding to the energy eigenvalue $E_{\vec{n}}$ of the system. Since Eq. (186) is a linear partial differential equation, the general solution of it is given by the linear combination of the types of the functions given by Eq. (187), i.e.

$$v_\beta = \sum_{\vec{n}} C_{\vec{n}}\, e^{-\beta E_{\vec{n}}}\, \Psi_{\vec{n}}(\vec{r}) \quad , \tag{189}$$

where $C_{\vec{n}}$'s are the coefficients of the linear combination. We find from Eqs. (189) and (187), finally

$$f_\beta(\alpha;\vec{r}) = e^{\beta\Phi(\vec{r})} \sum_{\vec{n}} C_{\vec{n}} e^{-\beta E_{\vec{n}}}\, \Psi_{\vec{n}}(\vec{r}) \quad . \tag{190}$$

Now, let us impose the boundary condition of the function f_β given by Eq. (177) on this solution of Eq. (190), to have

$$1 = \sum_{\vec{n}} C_{\vec{n}}\, \Psi_{\vec{n}}(\vec{r}).$$

We have, from this equation, formally

$$C_{\vec{n}} = \int_{V^N} d^{3N}\vec{r}\; \Psi^*_{\vec{n}}(\vec{r}) \tag{191}$$

by using the orthonormalization condition of the energy eigenfunction $\Psi_{\vec{n}}(r)$ given by

$$\int_{V^N} d^{3N}\vec{r}\ \Psi^*_{\vec{n}'}(\vec{r})\Psi_{\vec{n}}(\vec{r}) = \delta(\vec{n}',\vec{n}) \ . \qquad (191)'$$

The substitution of Eq. (191) into Eq. (190) gives us

$$f_\beta = e^{\beta\Phi(\vec{r})} \sum_{\vec{n}} e^{-\beta E_{\vec{n}}} [\int_{V^N} d^{3N}\vec{r}'\Psi^*_{\vec{n}}(\vec{r}')]\Psi_{\vec{n}}(\vec{r}). \qquad (192)$$

This is the formal form of the function f_β corresponding to the neglection of the unlucky term of Eq. (184). We can, then, find the Neumann's density matrix $D_\beta(\vec{r},\vec{r})$ by combining Eqs. (192), (165), and (155), and then using

$$\int_\infty d^{3N}\vec{k}\, e^{-\alpha\beta\vec{k}^2 + i\vec{k}\cdot(\vec{r}-\Pi\vec{r})} = (\frac{2\pi}{\lambda})^{3N} e^{-\pi(\vec{r}-\Pi\vec{r})^2/\lambda^2} \ , \qquad \text{(AIII)} \qquad (193)$$

where the quantity λ is defined in Eq. (157).

It is as follows:

$$D^{\pm}_\beta(\vec{r},\vec{r}) = e^{\beta F^{\pm}_\beta} \sum_{\vec{n}} e^{-\beta E_{\vec{n}}} \boxed{(\int_{V^N} d^{3N}\vec{r}'\Psi^*_{\vec{n}}(\vec{r}')) \sum_{\Pi} \frac{(\pm 1)^\Pi}{N!\lambda^{3N}} e^{-\pi(\vec{r}-\Pi\vec{r})^2/\lambda^2}} \Psi_{\vec{n}}(\vec{r}) \qquad (194)$$

Now, let us find the exact formal form of the Neumann's density matrix $D_\beta(\vec{r},\vec{r})$ in terms of the complete set of the energy eigenfunctions $\Psi_{\vec{n}}$'s. This can be done easily by inserting the identity I of Eq. (31) between the bra vector $\langle\vec{r}|$ and the operator D_β in Eq. (98) with $\vec{r}' = \vec{r}$, and referring to the definition of $\Psi_{\vec{n}}(\vec{r})$ immediately above Eq. (136). It is , then, as follows:

$$D^{\pm}_\beta(\vec{r},\vec{r}) = [\sum_{\vec{n}} e^{-\beta E_{\vec{n}}}]^{-1} \sum_{\vec{n}} e^{-\beta E_{\vec{n}}} \Psi^*_{\vec{n}}(\vec{r})\Psi_{\vec{n}}(\vec{r}) \ . \qquad (195)$$

We see, thus on comparing Eq. (195) with Eq. (194), that the neglection of the term of Eq. (184) is equivalent to approximating the complex conjugate $\Psi^*_{\vec{n}}(\vec{r})$ of the energy eigenfunction to the function inside of the dot rectangle [------] in Eq. (194), i.e.

$$\Psi^*_{\vec{n}}(\vec{r}) \cong \left(\int_{V^{3N}} d^{3N}\vec{r}\,' \Psi^*_{\vec{n}}(\vec{r}\,')\right) \sum_{\Pi} \frac{(\pm 1)^{\Pi}}{N!\lambda^{3N}} e^{-\pi(\vec{r}-\Pi\vec{r})^2/\lambda^2} . \qquad (195)'$$

This implies that the complex conjugate $\Psi^*_{\vec{n}}(\vec{r})$ for every possible lattice vector $\vec{n}$ of quantum number is approximated by the Neumann's density matrix of quantum ideal fluid given by Eq. (157) within their different constant-coefficients. Furthermore, this approximation of the right-hand side of Eq. (195)' may become a function given by the product of the real function and complex constant, which can make the approximated density matrix of Eq. (194) be complex in non-consistence with the realistic physical menaing of the Neumann's density matrix. There is also a possibility leading to a serious difficulty that the integral given by Eq. (191) is divergent even if the normalization of Eq. (191)' is satisfied. Thus, it is very dangerous to neglect the term given by Eq. (184) in Eq. (183), even though it is an unlucky term desirable to be neglected.

Now, we want to return to the discussion of solving our basic equation given by Eq. (183). We are going to find the solution $f_\beta(\alpha;\vec{k},\vec{r})$ in its series expansion form of the parameter α, or β contained in it. Before we develop our theory of the solution f_β, we examine, at first, the numerical characters of α and β for the sake of our intuitive foresight into the convergence of the series expansion

form of the solution f_β to be assumed in advance. The parameter defined by Eq. (163) has the dimension given by

$$[\alpha] = [ML^4T^{-2}] = [\text{energy}][\text{length}]^2 = [\text{erg cm}^2] ,$$

and its numerical vlaue depends upon the mass of the particle under consideration with the inverse proportionality of the mass. For example, for the elctron, proton and Ne-atom, they are roughly as follows:

$$\alpha = 5.5\text{x}10^{-28} \text{ for } e^-;\ 3.0\text{x}10^{-31} \text{ for p};\ 1.8\text{x}10^{-32} \text{ for Ne},$$

where the unit of α has taken as "erg cm^2". It is noticeable that we have, for Ne-atom, numerically

$$\alpha \doteqdot k^2(\doteqdot 1.9\text{x}10^{-32}) .$$

The parameter β defined by Eq. (49) has the dimension given by

$$[\beta] = [M^{-1}L^{-2}T^2] = [\text{energy}]^{-1} = [\text{erg}^{-1}] ,$$

and its numerical value is given roughly by

$$\beta \doteqdot 7.2\text{x}10^{15}/T \quad (\text{erg}^{-1}) .$$

The numerical value of $\alpha\beta$ is therefore roughly as follows:

$$\alpha\beta \doteqdot 4.0\text{x}10^{-12}/T \text{ for } e^-;\ 2.2\text{x}10^{-15}/T \text{ for p};\ 1.3\text{x}10^{-16}/T \text{ for Ne}$$

with the dimension and unit given by

$$[\alpha\beta] = [L^2] = [\text{area}] = [\text{cm}^2] .$$

Since the numerical value of α is very small as shown above, the

following Maclaurin's expansion[26] is possible for an analytic potential function $\Phi(\vec{r})$ and a specified value of β ($\neq\infty$):

$$f_\beta(\alpha;\vec{k},\vec{r}) = \sum_{n=0}^{\infty} f_\beta^{(n)}(\vec{k},\vec{r})\alpha^n, \tag{196}$$

where we have put

$$f_\beta^{(n)}(\vec{k},\vec{r}) \equiv (\partial_\alpha^n f_\beta)_{\alpha=0}/n! \quad .$$

Now, let us look at Eq. (166) with putting $\alpha = 0$. We have, then $(\Omega_\beta)_{\alpha=0} = I$ (identity), so that

$$f_\beta^{(0)}(\vec{k},\vec{r}) \equiv f_\beta(0;\vec{k},\vec{r}) = 1. \tag{197}$$

The power series of α given by Eq. (196) takes, therefore by virtue of Eq. (197), the following form:

$$f_\beta(\alpha;\vec{k},\vec{r}) = 1 + \sum_{n=1}^{\infty} f_\beta^{(n)}(\vec{k},\vec{r})\alpha^n. \tag{198}$$

Formally, it seems, from the above discussions, that this expansion never make any trouble in our subsequent theory. We will see, in the power series determination of the diagonal element of the Neumann's density matrix $D_\beta(\vec{r},\vec{r}')$ in the next section, that this expansion is not quite good enough at low-temperature region. It will turn out that this unfortunate trouble is made by the so-called unlucky term given by Eq. (184). Therefore, it is desirable to give up our further discussion.

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[26] We must, in general, assume the Laurent's expansion given by the form $\sum_{n=-\infty}^{\infty} c_n \alpha^n$. However, this general expansion goes to the Maclaurin's expansion in our case of f_β since f_β has no pole at $\alpha = 0$ and it is finite at $\alpha = 0$ as will be shown in Eq. (197).

However, it is valuable to show concretely the origin of the disadvantage of this kind of expansion theory to the reader for the sake of his reference which makes him have a new and better idea of this problem without his unfortunate loss of time.

Let us substitute, now, Eq. (198) into Eq. (183). We have, then after some rearrangements,

$$\sum_{n=1}^{\infty} \partial_\beta f_\beta^{(n)} \alpha^n = \alpha[\beta^2(\vec{\partial}\Phi)^2 - 2i\beta\vec{k}\cdot\vec{\partial}\Phi - \beta\vec{\partial}^2\Phi]$$

$$+ \sum_{n=2}^{\infty} \alpha^n [\vec{\partial}^2 f_\beta^{(n-1)} - 2\beta\vec{\partial}\Phi\cdot\vec{\partial} f_\beta^{(n-1)} - \beta(\vec{\partial}^2\Phi) f_\beta^{(n-1)}$$

$$+ \beta^2(\vec{\partial}\Phi)^2 f_\beta^{(n-1)} + 2i\vec{k}\cdot\vec{\partial} f_\beta^{(n-1)} - 2i\beta\vec{k}\cdot(\vec{\partial}\Phi) f_\beta^{(n-1)}], \tag{199}$$

with the boundary condition given by

$$[f_\beta^{(n)}(\vec{k},\vec{r})]_{\beta=0} = 0, \quad (n\neq 0), \tag{200}$$

which comes from the use of Eq. (177) for Eq. (198). The comparison of the coefficients of the same power of α on both-hand sides of Eq. (199) gives us

$$\left.\begin{aligned} \partial_\beta f_\beta^{(1)} &= \beta^2(\vec{\partial}\Phi)^2 - 2i\beta\vec{k}\cdot\vec{\partial}\Phi - \beta\vec{\partial}^2\Phi, \\ \partial_\beta f_\beta^{(n)} &= \beta^2(\vec{\partial}\Phi)^2 f_\beta^{(n-1)} - 2i\beta\vec{k}\cdot(\vec{\partial}\Phi) f_\beta^{(n-1)} - \beta(\vec{\partial}^2\Phi) f_\beta^{(n-1)} \\ &\quad + \vec{\partial}^2 f_\beta^{(n-1)} - 2\beta\vec{\partial}\Phi\cdot\vec{\partial} f_\beta^{(n-1)} + 2i\vec{k}\cdot\vec{\partial} f_\beta^{(n-1)}, \\ &\quad (n=2,3,4,\ldots) . \end{aligned}\right\} \tag{201}$$

We integrate this iteration differential equation of Eq. (201) with respect to the parameter β with the iteration procedure under the condition of Eq. (200). We have, then, the following result:

$$
\left.
\begin{aligned}
f_{\beta}^{(1)} &= \frac{\beta^3}{3}(\vec{\partial}\Phi)^2 - \frac{\beta^2}{2}\vec{\partial}^2\Phi - i\beta^2\vec{k}\cdot\vec{\partial}\Phi, \\
f_{\beta}^{(2)} &= \left[\frac{\beta^6}{18}(\vec{\partial}\Phi\cdot\vec{\partial}\Phi)^2 - \frac{\beta^5}{30}\left\{5(\vec{\partial}\Phi)^2(\vec{\partial}^2\Phi) + 4\vec{\partial}\Phi\cdot\vec{\partial}(\vec{\partial}\Phi)^2\right\}\right. \\
&\quad + \frac{\beta^4}{24}\left\{3(\vec{\partial}^2\Phi)^2 + 2\vec{\partial}^2(\vec{\partial}\Phi)^2 + 6\vec{\partial}\Phi\cdot\vec{\partial}(\vec{\partial}^2\Phi)\right\} \\
&\quad \left. - \frac{\beta^3}{6}\vec{\partial}^2\vec{\partial}^2\Phi + \frac{2\beta^3}{3}\vec{k}\cdot(\vec{\partial}\vec{\partial}\Phi\cdot\beta\vec{\partial}\Phi\vec{\partial}\Phi)\cdot\vec{k}\right] \\
&\quad - i\vec{k}\cdot\left[\frac{\beta^5}{3}(\vec{\partial}\Phi)(\vec{\partial}\Phi)^2 + \frac{\beta^4}{6}\left\{(\vec{\partial}\vec{\partial}\Phi)\cdot\vec{\partial}\Phi - 3\vec{\partial}\Phi(\vec{\partial}^2\Phi)\right\}\right],
\end{aligned}
\right\} \quad (202)
$$

and so on.

The substitution of Eq. (202) into Eq. (198) makes us know the power series form of the function f_{β} up to its third term, i.e

$$f_{\beta} = 1 + \alpha f_{\beta}^{(1)}(\vec{k},\vec{r}) + \alpha^2 f_{\beta}^{(2)}(\vec{k},\vec{r}) + \ldots \qquad (203)$$

with the expression given by Eq. (202). It can be, by doing a rearrangement of Eq. (202) so as to make it be in the form of the power series in β, shown that this expansion is equal actually to the expansion given by Eq. (176). As shown in Eq. (202), we have not any difficulty in this expansion theory if we can prove only that

$$\lim_{n\to\infty}\left[\,|f_{\beta}^{(n+1)}(\vec{k},\vec{r})| \div |f_{\beta}^{(n)}(\vec{k},\vec{r})|\,\right] < \frac{1}{\alpha}\,(\doteq 2.678\times 10^{54}\,\mathrm{m}) \qquad (204)$$

at every point $(\vec{k},\vec{r})$ of the phase space for a given value of β and a given analytic potential function $\Phi(\vec{r})$.[27] However, as stated already, this expansion expression has a serious disadvantage even not at so low temperature. It seems that this disadvantage probably comes from our careless manipulation of the basic equation of Eq. (183) without any investigation of the numerical estimates for the quantities other than the parameters α and β, in setting up the iteration differential equation given by Eq. (201). Next, we will set up another kind of iteration differential equation from the basic equation given by Eq. (183) on the basis of the following numerical estimation:

This numerical estimation will be done exclusively for Ne-fluid since we want to apply our expansion theory to the Ne-quantum fluid, and compare it with the experimental result, in order to see how much it is correct. Following Uhlenbeck and Beth,[28] we assume, in Eq. (183), that the quantities given by

$$\vec{\partial}^2 f_\beta,\ \vec{\partial}\Phi\cdot\vec{\partial} f_\beta,\ (\vec{\partial}^2\Phi) f_\beta,\ (\vec{\partial}\Phi\cdot\vec{\partial}\Phi) f_\beta,\ (\vec{\partial}\Phi) f_\beta, \vec{\partial} f_\beta$$

are in the same order of their numerical magnitudes.[28] For the numerical estimation of the propagation vector $\vec{k}_\lambda$, or momentum $\vec{p}_\lambda (=\hbar\vec{k}_\lambda)$ of each Ne-atom (a rare monoatomic molecule), we may apply the generalized equipartition theorem of classical statistical mechanics,[36] since it

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[27] This is the Cauchy's ratio test for the absolute convergency of the power series. Other test may be applicable. However, as Kramers has pointed out even before, there is, at least at present, no way to have a clear test of the convergency of this series.

[28] They did not have this assumption explicitly. But their paper has shown that they have recognized it tacitly.

gives the answer of first order approximation of quantum statistical mechanics and the most probable value of $\vec{k}_\lambda$ may be determined from the result obtained by this generalized equipartition theorem. We have, thus,

$$\alpha\vec{k}_\lambda^2 = \vec{p}_\lambda^2/2m \sim 3KT/2 = 3/2\beta ,$$

or

$$|\vec{k}_\lambda| \sim 1/\sqrt{\alpha\beta} .$$

Hence, for the temperature interval $25^oK < T < 100^oK$, we see the following numerical estimations:

$$\alpha\beta^2 \fallingdotseq 1/T^2 \Rightarrow 10^{-4} \sim 1.6\times10^{-3}; \quad \alpha\beta|\vec{k}_\lambda| \fallingdotseq T^{-\frac{1}{2}} \Rightarrow 0.1 \sim 0.2$$

$$\alpha\beta \fallingdotseq K/T \Rightarrow 1.3\times10^{-18} \sim 5.2\times10^{-18}; \quad \alpha|\vec{k}_\lambda| \fallingdotseq KT^{\frac{1}{2}} \Rightarrow 1.3\times10^{-17} \sim 7.5\times10^{-16} .$$

The first two and the second two may be regarded roughly as the same order of numerical magnitude respectively. But we may regard $\alpha\beta|\vec{k}_\lambda|$ as being most dominant. Correspondingly, the most dominant term in Eq. (183) is the so-called unlucky term given by

$$2i\alpha\beta\vec{k}\cdot(\vec{\partial}\Phi)f_\beta, \text{ or } i(2\alpha\beta/\hbar)(\vec{p}\cdot\vec{\partial}\Phi)f_\beta ,$$

by using the de Broglie's relationship $\vec{p} = \hbar\vec{k}$. In this way, the dominant term is characterized by the small quantity $\hbar$ appearing in its demoninator by introducing the momentum $\vec{p}$ in place of the propagation vector $\vec{k}$ of the system. This fact tells us that the use of the momentum representation $|\vec{p}\rangle$ is more convenient and troubleless than that of the propagation vector representation $|\vec{k}\rangle$, at least, in the practical calculation of the problem of the Ne quantum fluid at low temperature. In this case, Eqs.(153) and

(155) are modified simply by

$$F'_{\beta}(\vec{p},\vec{r}) = e^{-i\vec{p}\cdot\vec{r}/\hbar}e^{-\beta H_e}e^{i\vec{p}\cdot\vec{r}/\hbar},$$

$$D^{\pm}_{\beta}(\vec{r},\vec{r}) = \frac{\exp(\beta F^{\pm}_{\beta})}{N!h^{3N}}\sum_{\Pi}(\pm 1)^{\Pi}\int_{\infty} d^{3N}_{pe}\, e^{i\vec{p}\cdot(\vec{r}-\Pi\vec{r})/\hbar}F'_{\beta}(\vec{p},\vec{r}) \quad , \tag{205}$$

where h is the planck constant given by $h = 2\pi\hbar$. However, since we have $\hbar\propto\sqrt{\alpha}$, we can proceed our theory without any further modification simply by putting

$$z \overset{def}{=} \sqrt{\alpha}, \quad \text{or} \quad \alpha = z^2, \tag{205}'$$

and

$$\vec{\xi} = z\vec{k} \tag{205}''$$

in our basic equation given by Eq. (183). We obtain, then, the following modified basic equation:

$$\boxed{\begin{aligned}\partial_{\beta}f_{\beta} = {} & -2i\beta z\vec{\xi}\cdot(\vec{\partial}\Phi)f_{\beta} + z^2\beta^2(\vec{\partial}\Phi)^2 f_{\beta} + 2iz\vec{\xi}\cdot\vec{\partial}f_{\beta} \\ & -z^2\beta(\vec{\partial}^2\Phi)f_{\beta} - 2z^2\beta\vec{\partial}\Phi\cdot\vec{\partial}f_{\beta} + z^2\vec{\partial}^2 f_{\beta} \quad .\end{aligned}} \tag{206}$$

Of course, this is the exact equation for the exact function $f_{\beta}(\vec{\xi},\vec{r})$. We expand this function in the following form of the power series in z:

$$f_{\beta} = \sum_{n=0}^{\infty} z^n f_{\beta}^{(n)}(\vec{\xi},\vec{r}) = 1 + \sum_{n=1}^{\infty} z^n f_{\beta}^{(n)}(\vec{\xi},\vec{r}) \ ^{29} \tag{207}$$

with the boundary condition given still by Eqs. (200) and (197). We

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[29] This Maclaurin's expansion is possible at a point $(\vec{\xi},\vec{r})$ of the phase space for an analytic potential function $\Phi(\vec{r})$ and a given value of the parameter β under the assumption similar to Eq. (204), since z is given by the small value $z \equiv \sqrt{\alpha} \sim 4\times 10^{-17}$ for the Ne quantum fluid.

substitute Eq. (207) into Eq. (206). We have, then,

$$\sum_{n=1}^{\infty} z^n \partial_\beta f_\beta^{(n)} = \sum_{n=1}^{\infty} z^n [\beta^2 (\vec{\partial}\Phi)^2 f_\beta^{(n-2)} - \beta(\vec{\partial}^2\Phi) f_\beta^{(n-2)}$$

$$- 2\beta\vec{\partial}\Phi\cdot\vec{\partial} f_\beta^{(n-2)} + \vec{\partial}^2 f_\beta^{(n-2)} - 2i\beta\vec{\xi}\cdot(\vec{\partial}\Phi) f_\beta^{(n-1)}$$

$$+ 2i\vec{\xi}\cdot\vec{\partial} f_\beta^{(n-1)}], \tag{208}$$

by referring to the boundary condition of Eq. (197), i.e. $f_\beta^{(0)} = 1$ and defining newly $f_\beta^{(-1)} = 0$. We obtain, thus on comparing the terms of the same power of z on both-hand sides in Eq. (208), the following iteration-equation:

$$\partial_\beta f_\beta^{(n)} = \beta^2 (\vec{\partial}\Phi)^2 f_\beta^{(n-2)} - \beta(\vec{\partial}^2\Phi) f_\beta^{(n-2)} - 2\beta\vec{\partial}\Phi\cdot\vec{\partial} f_\beta^{(n-2)}$$

$$+ \vec{\partial}^2 f_\beta^{(n-2)} - 2i\beta\vec{\xi}\cdot(\vec{\partial}\Phi) f_\beta^{(n-1)} + 2i\vec{\xi}\cdot f_\beta^{(n-1)}, \tag{209}$$

$$(f_\beta^{(-1)} \equiv 0,\ f_\beta^{(0)} = 1,\ n = 1,2,3,4,\ldots).$$

We observe here that this iteration-equation is equal formally to the second of Eq. (201) with a different starting equation. The starting equation of Eq. (209) is written explicity as

$$\partial_\beta f_\beta^{(1)} = -2i\beta\vec{\xi}\cdot\vec{\partial}\Phi\ . \tag{210}$$

We integrate Eq. (209) with respect to the parameter β starting with Eq. (210) under the boundary condition given by Eq. (200). It follows then after some tedious though straightforward calculations that

$$f_\beta^{(1)} = -i\beta^2 \vec{\xi}\cdot\vec{\partial}\Phi,$$

$$f_\beta^{(2)} = (\tfrac{1}{3}\beta^3\vec{\partial}\Phi\cdot\vec{\partial}\Phi - \tfrac{1}{2}\beta^2\vec{\partial}^2\Phi) - \vec{\xi}\vec{\xi}:(\tfrac{1}{2}\beta^4\vec{\partial}\Phi\vec{\partial}\Phi - \tfrac{2}{3}\beta^3\vec{\partial}\vec{\partial}\Phi),$$

$$f_\beta^{(3)} = -i\vec{\xi}\cdot[\tfrac{1}{3}\beta^5\vec{\partial}\Phi\vec{\partial}\Phi\cdot\vec{\partial}\Phi - \tfrac{1}{6}\beta^4(3\vec{\partial}\Phi\vec{\partial}^2\Phi + 5\vec{\partial}\vec{\partial}\Phi\cdot\vec{\partial}\Phi) + \tfrac{2}{3}\beta^3\vec{\partial}\vec{\partial}^2\Phi]$$

$$i\vec{\xi}\vec{\xi}\vec{\xi}\vdots(\tfrac{1}{6}\beta^6\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}\Phi - \tfrac{2}{3}\beta^5\vec{\partial}\vec{\partial}\Phi\vec{\partial}\Phi + \tfrac{1}{3}\beta^4\vec{\partial}\vec{\partial}\vec{\partial}\Phi),$$

$$f_\beta^{(4)} = [\tfrac{1}{18}\beta^6(\vec{\partial}\Phi\cdot\vec{\partial}\Phi)^2 - \tfrac{1}{30}\beta^5(5\vec{\partial}\Phi\cdot\vec{\partial}\Phi\vec{\partial}^2\Phi + 8\vec{\partial}\Phi\cdot\vec{\partial}\vec{\partial}\Phi\cdot\vec{\partial}\Phi)$$

$$+ \tfrac{1}{24}\beta^4(3\vec{\partial}^2\Phi\vec{\partial}^2\Phi + 10\vec{\partial}\Phi\cdot\vec{\partial}\vec{\partial}^2\Phi + 4\vec{\partial}\vec{\partial}\Phi:\vec{\partial}\vec{\partial}\Phi) - \tfrac{1}{6}\beta^3\vec{\partial}^4\Phi]$$

$$- \vec{\xi}\vec{\xi}:[\tfrac{1}{6}\beta^7\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}\Phi\cdot\vec{\partial}\Phi - \beta^6(\tfrac{3}{5}\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}^2\Phi + \tfrac{2}{9}\vec{\partial}\vec{\partial}\Phi\vec{\partial}\Phi\cdot\vec{\partial}\Phi + \tfrac{13}{6}\vec{\partial}\vec{\partial}\Phi\cdot\vec{\partial}\Phi\vec{\partial}\Phi)$$

$$+ \beta^5(\tfrac{13}{15}\vec{\partial}\vec{\partial}\Phi\vec{\partial}^2\Phi + \tfrac{7}{3}\vec{\partial}\vec{\partial}\vec{\partial}\Phi\cdot\vec{\partial}\Phi + \tfrac{14}{15}\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}^2\Phi + \tfrac{1}{3}\vec{\partial}\vec{\partial}\Phi\cdot\vec{\partial}\vec{\partial}\Phi - \tfrac{1}{6}\beta^4\vec{\partial}\vec{\partial}\vec{\partial}^2\Phi]$$

$$+ \vec{\xi}\vec{\xi}\vec{\xi}\vec{\xi}\vdots(\tfrac{1}{24}\beta^8\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}\Phi - \tfrac{5}{42}\beta^7\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}\Phi - \tfrac{1}{9}\beta^6\vec{\partial}\vec{\partial}\Phi\vec{\partial}\Phi\vec{\partial}\Phi + \tfrac{1}{15}\beta^5\vec{\partial}\vec{\partial}\vec{\partial}\vec{\partial}\Phi), \tag{211}$$

and so on. The general formal form of the coefficient function $f_\beta^{(n)}$ of Eq. (207) can be easily guessed from the regular character of Eq. (211). The mathematical meaning of the notations given by :, ⋮, and ⋮, etc. can be understood easily by referring to the footnote (23). Our reason for not carrying out the calculations to obtain the other coefficient functions $f_\beta^{(n)}$, (n≠5,6,7,...) of higher order than Eq. (211) is in our belief that the quantum effect of the Ne fluid may be detected by the second order approximation which will be presented in the next section.

The substitution of Eq. (211) into Eq. (207) gives us finally the power series form of the function f_β up to its 5^{th} term, i.e.

$$f_\beta = 1 + zf_\beta^{(1)}(\vec{\xi},\vec{r}) + z^2 f_\beta^{(2)}(\vec{\xi},\vec{r}) + z^3 f_\beta^{(3)}(\vec{\xi},\vec{r}) + z^4 f_\beta^{(4)}(\vec{\xi},\vec{r}) + \ldots \qquad (212)$$

with the expression given by Eq. (211). We have, thus, obtained 3 types of expansions of the function f_β given by Eqs. (212), (203), and (176) in our formalism. However, all of these expansions are nothing but the appropriate rearrangements of the same power series of the two parameters α and β given by the following Maclaurin's power series of two independent variables:

$$f(\alpha,\beta;\vec{k},\vec{r}) = [\exp(\alpha\partial_\alpha + \beta\partial_\beta)]f(0,0;\vec{k},\vec{r}), \qquad (213)$$

where we have abbreviated as follows:

$$f_\beta(\alpha;\vec{k},\vec{r}) \equiv f(\alpha,\beta;\vec{k},\vec{r}),\ \exp(\alpha\partial_\alpha + \beta\partial_\beta) \equiv \sum_{n=0}^{\infty} (\alpha\partial_\alpha + \beta\partial_\beta)^n/n!\ ,$$

$$\partial_\alpha^j \partial_\beta^\ell f(0,0;\vec{k},\vec{r}) = [\partial_\alpha^j \partial_\beta^\ell f_\beta(\alpha;\vec{k},\vec{r})](\alpha,\beta) = (0,0)\ .$$

Eq. (176) is the rearrangement of Eq. (213) in the power series form of the parameter β, while Eq. (203) and (212), in the parameters α and $\alpha^{\frac{1}{2}}$ respectively. In this sense, we may call our method the Maclaurin's expansion method in terms of parameters. In particular, the Maclaurin's expansion form given by Eq. (212), or Eq. (203) is the power series of the very small planck's constant h. This can be regarded as the power series expansion under the idea suggested first by Jeffreys(1924),

Wentzel(1926), Kramers(1926), and Brillouin(1926) in the theory of the solution of wave equation. Therefore, we call Eqs. (212) and (203) the expansion by the W.K.B.J. method, or simply the WKB method. Finally, it should be pointed out that Eq. (212) is correct only if it satisfies a certain condition of convergence, e.g. the Cauchy's condition:

$$\lim_{n\to\infty} [\,|f_\beta^{(n+1)}(\vec{\xi},\vec{r})|\div|f_\beta^{(n)}(\vec{\xi},\vec{r})|\,] < \frac{1}{z}(\doteqdot 1.256\times 10^{27}\,m^{\frac{1}{2}}) \qquad (214)$$

at every point $(\vec{\xi},\vec{r})$ of the phase space for the given analytic potential function $\Phi(\vec{r})$ and the given value of the parameter β.

In the next section, we will determine the power series forms of the diagonal element $D_\beta(\vec{r},\vec{r})$ of the Neumann's density matrix and the quantum pair correlation function $g_\beta(n;\vec{r}_1,\vec{r}_2)$ by using Eq. (212).

3.2. The Power Series Forms of the Diagonal Element of the Neumann's Density Matrix and the Quantum Pair Correlation Function

We are, at first, interested in showing that the serious disadvantage of the type of expansion given by Eq. (203) occurs even not at so low temperature region as stated already in the foregoing section. The substitution of Eq. (203) into Eq. (155) through Eq. (165) gives us

$$D_\beta^{\pm}(\vec{r},\vec{r}) = \frac{\exp(\beta F_\beta^{\pm})}{(2\pi)^{3N}N!}\sum_{\Pi}(\pm 1)^{\Pi}\int_{\infty} d^{3N}\vec{k}\, e^{i\vec{k}\cdot(\vec{r}-\Pi\vec{r})}e^{-\beta H_c}(1+\sum_{n=1}^{\infty}\alpha^n f_\beta^{(n)}(\vec{k},\vec{r})),$$

and the component of $D_\beta^{I}(\vec{r},\vec{r})$ corresponding to the identity element $I(=\Pi)$ of the symmetric group $\Phi(N)$ is

$$D'_\beta(\vec{r},\vec{r}) = \frac{\exp(\beta F_\beta)}{(2\pi)^{3N} N!} \int_\infty d^{3N}\vec{k}\; e^{-\beta H_c}\left(1+\sum_{n=1}^{\infty} \alpha^n f_\beta^{(n)}\right) .$$

The third term of this component is, with the omission of the normalization constant of $D_\beta^{\pm}(\vec{r},\vec{r})$, given by

$$\alpha^2 J^{(2)} \tag{215}$$

with the definition given by

$$J^{(2)} \underset{\equiv\equiv}{\text{def}} \cdot \int_\infty d^{3N}\vec{k}\; e^{-\beta H_c} f_\beta^{(2)}(\vec{k},\vec{r}). \tag{216}$$

Now, let us look again at the explicit expression of the function $f_\beta^{(2)}(\vec{k},\vec{r})$ given by Eq. (202). The terms resulting from the so-called unlucky term of Eq. (184) are the last two terms involving the propagation vector $\vec{k}$. The one(imaginary) among these last two terms does not give a contribution to the integral of Eq. (216) in accordance with its odd character in $\vec{k}$. We calculate the contribution of the remaining term to the integral of Eq. (216), i.e.

$$\frac{2}{3}\beta^3 \int_\infty d^{3N}\vec{k}\; e^{-\beta\Phi(\vec{r})-\alpha\beta\vec{k}^2} \vec{k}\cdot(\vec{\partial}\vec{\partial}\Phi - \beta\vec{\partial}\Phi\vec{\partial}\Phi)\cdot\vec{k},$$

which is equal to

$$= (\beta^2/3\alpha) \int_\infty d^{3N}\vec{k}\; e^{-\beta H_c}(\vec{\partial}^2\Phi - \beta\vec{\partial}\Phi\cdot\vec{\partial}\Phi), \tag{217}$$

by using a formula given by

$$\int_\infty d^{3N}k\, e^{-\alpha\beta\vec{k}^2} \vec{k}\cdot\overleftrightarrow{\equiv}\cdot\vec{k} = \frac{1}{2\alpha\beta}\int_\infty d^{3N}\vec{k}\; e^{-\alpha\beta\vec{k}^2} \mathrm{Tr}(\overleftrightarrow{\equiv}) \tag{AIV}$$

$$\left(\overleftrightarrow{\equiv} = \text{a diadic not dependent on } \vec{k}\right). \tag{218}$$

Eq. (217) with a coefficient $\beta^2/3\alpha$ is very large compared with any other part of Eq. (216) as long as we have not a small value of β comparable with the very small microscopic-constant α, i.e. high temperature, or the combination of Eq. (217) with Eq. (215) makes this part be put in the first order term of α. It is seen easily that the same situation occurs in the 3rd, 4th, ... order terms of α. In fact, we are concerned with the calculation of an infinite number of terms even only in the knowledge of the first order term of α. This disadvantage disappears if we use our last expansion form given by Eq. (212). We will show this below.

Let us substitute Eq. (212) into Eq. (155) through Eq. (165), to have

$$D_\beta^{\pm}(\vec{r},\vec{r}) = \frac{\exp(\beta F_\beta^{\pm})}{(2\pi)^{3N}N!} \sum_{\Pi} (\pm 1)^{\Pi} \int d^{3N}\vec{k}\; e^{i\vec{k}\cdot(\vec{r}-\Pi\vec{r})-\beta H_c}$$

$$\cdot \left[1+\sum_{n=1}^{\infty} z^n f_\beta^{(n)}(\vec{\xi},\vec{r})\right] \tag{219}$$

by assuming the convergency of this power series form. We rewrite, for the convenience of our subsequent calculations, Eq. (219) in the following form:

$$D_\beta^{\pm}(\vec{r},\vec{r}) = \frac{\exp(\beta F_\beta^{\pm})}{(2\pi)^{3N}N!} \sum_{n=0}^{\infty} z^n D_\beta^{(n)}(\vec{r})^{\pm} \tag{220}$$

with the definition given by

$$D_\beta^{(n)}(\vec{r})^{\pm} \overset{\text{def.}}{=\!=} \sum_{\Pi} (\pm 1)^{\Pi} \int d^{3N}\vec{k}\; e^{i\vec{k}\cdot(\vec{r}-\Pi\vec{r})-\beta H_c} f_\beta^{(n)}(\vec{\xi},\vec{r}). \tag{221}$$

We calculate these integrals by using Eq. (211). The first integral is

$$D_\beta^{(0)}(\vec{r})^{\pm} = e^{-\beta\Phi(\vec{r})}\sum_{\Pi}(\pm 1)^{\Pi}\int d^{3N}\vec{k}\; e^{-\alpha\beta\vec{k}^2+i\vec{k}\cdot(\vec{r}-\Pi\vec{r})} \quad , \tag{222}$$

by replacing the classical Hamiltonian $H_c(\vec{k},\vec{r})$ by its explicit form given by the first of Eq. (166) and using $f_\beta^{(0)}(\vec{\xi},\vec{r}) \equiv 1$, and calculated as

$$D_\beta^{(0)}(\vec{r})^{\pm} = (\pi/\alpha\beta)^{3N/2}\sum_{\Pi}(\pm 1)^{\Pi}\exp[-\beta\Phi(\vec{r})-(\vec{r}-\Pi\vec{r})^2/(4\alpha\beta)] \tag{223}$$

by using the formula given by Eq. (193) with the replacement of

$$\lambda = \sqrt{4\pi\alpha\beta}. \tag{224}$$

The summation in Eq. (223) goes over all elements of N! in number in the symmetric group. For N large enough, the total number N! of its elements is given asymptotically by the Stirling formula of

$$N! = N^N e^{-N}\sqrt{2\pi N}\left(1 + \frac{1}{12N} + \frac{1}{288N^2} - \frac{139}{51840N^3} - \ldots\right) \tag{225}$$

which is almost ∞.[37] Eq. (223) may be expressed also alternatively by

$$D_\beta^{(0)\pm}(\vec{r}) = (\pi/\alpha\beta)^{3N/2}\exp[-\beta\{\Phi(\vec{r})+U_0^{\pm}(\alpha,\beta;\vec{r})\}] \quad , \tag{226}$$

by defining a potential $U_0^{\pm}(\alpha,\beta;\vec{r})$ with two parameters α and β:

$$U_0^{\pm}(\alpha,\beta;\vec{r}) \stackrel{\text{def.}}{=\!=} -\ell n[1 + \sum_{\Pi}{}' (\pm 1)^{\Pi}\, e^{-(\vec{r}-\Pi\vec{r})^2/(4\alpha\beta)}]^{1/\beta} \quad , \tag{227}$$

where the summation Σ' goes over all Π except $\Pi = I$. Obviously, this new potential $U_0^{\pm}(\alpha,\beta;\vec{r})$ occurs because of the exchange of identical, indistinguishable particles of the system under consideration.

This potential varies with the values of two parameters α and β. That is, it is dependent upon the mass of single particle, the temperature of the system, and simply the distance between every pair of two particles. This apparent potential part disappears at extremely high temperature ($\beta \to 0$), i.e.

$$\lim_{\beta \to 0} \beta U_0^{\pm}(\alpha, \beta; \vec{r}) = 0, \tag{228}$$

and acts more effectively with the decrease of the temperature and the mass of the single particle of the system showing the different features in a boson and fermion systems. In this sense, we may call this potential of Eq. (227) the total exchange effective potential of the system at a temperature specified by the parameter β. It should be noted that this exchange effective potential is the same as that of the ideal quantum-fluid as shown already in Eq. (157). Since we can change the part inside of [ ] of Eq. (227) into the following form:

$$\sum_{\Pi} (\pm 1)^{\Pi} e^{-(\vec{r} - \Pi\vec{r})^2/(4\alpha\beta)} = e^{-\vec{r}^2/(2\alpha\beta)} \sum_{\Pi} (\pm 1)^{\Pi} e^{\vec{r} \cdot (\Pi\vec{r})/(2\alpha\beta)}$$

by using the unitary property of every element Π of the symmetric group, the exchange effective potential is expressed also formally in the following determinantal (or permanantal) form:

$$U_0^{\pm}(\alpha, \beta; \vec{r}) = \frac{\vec{r}^2}{2\alpha\beta^2} - \frac{1}{\beta} \ell n \, \det\left(e^{\vec{r}_\lambda \cdot \vec{r}_\mu/(2\alpha\beta)}\right)_{\pm} , \tag{229}$$

$$(\lambda, \mu = 1, 2, 3, \ldots, N),$$

where the subscript "+" or "−" represents the "permanantal" or "determinantal" form respectively.

The second integral of Eq. (221) is, with the use of the first of Eqs. (211) and (205)", given by

$$D_\beta^{(1)\pm}(\vec{r}) = -i\beta^2 z e^{-\beta\Phi(\vec{r})} \sum_{\Pi} (\pm 1)^{\Pi} \int_\infty d^{3N}\vec{k}_e \, e^{-\alpha\beta\vec{k}^2 + i\vec{k}\cdot(\vec{r}-\Pi\vec{r})} \vec{k}\cdot\vec{\partial}\Phi(\vec{r}),$$

which is integrated out to

$$D_\beta^{(1)\pm}(\vec{r}) = \left(\frac{\pi}{\alpha\beta}\right)^{3N/2} \cdot \left(\frac{\beta z}{2\alpha}\right) \sum_{\Pi} (\pm 1)^{\Pi} e^{-\beta\Phi(\vec{r}) - (\vec{r}-\Pi\vec{r})^2/(4\alpha\beta)} (\vec{r}-\Pi\vec{r})\cdot\vec{\partial}\Phi(\vec{r}), \tag{230}$$

by using the formula given by

$$\int_\infty d^{3N}\vec{x}_e \, e^{-\alpha\beta\vec{x}^2} \left(\prod_{\lambda=1}^{3N} x_\lambda^{n_\lambda} \right) \equiv (\sqrt{\alpha\beta})^{3N - \sum_{\lambda=1}^{3N} n_\lambda} \cdot \prod_{\lambda=1}^{3N} \Gamma\left(\frac{n_\lambda}{2} + \frac{1}{2}\right) \sum_{j=0}^{\infty} \delta(n_\lambda, 2j), \tag{AIV}$$

$$\tag{231}$$

where $\delta(n_\lambda, 2j)$ is Kronecker's δ, and the Euler's Γ-function is given by

$$\Gamma\left(\frac{n_\lambda}{2} + \frac{1}{2}\right) \equiv \begin{cases} \pi \cdot n_\lambda! / [(n_\lambda/2)!] 2^{n_\lambda}, & \text{for an even positive interger } n_\lambda, \\ \left(\frac{n_\lambda}{2} - \frac{1}{2}\right)!, & \text{for an odd positive integer } n_\lambda. \end{cases}$$

In this way, we can, by using Eqs. (231), (211), and (205)", determine also the remainded integrals, i.e.

$$D_\beta^{(2)\pm}(\vec{r}),\ D_\beta^{(3)\pm}(\vec{r}),\ D_\beta^{(4)\pm}(\vec{r}),\ \text{etc.}$$

Thus, we obtain finally the following exact power series form of the diagonal element of the Neumann's density matrix:

$$D_\beta^{\pm}(\vec{r},\vec{r}) = \frac{\exp(\beta F_\beta^{\pm})}{(4\pi\alpha\beta)^{3N/2}} \cdot \frac{\exp[-\beta\Phi(\vec{r})]}{N!} \cdot \sum_{\Pi} (\pm 1)^{\Pi} \exp[-\frac{(\vec{r}-\Pi\vec{r})^2}{4\alpha\beta}] \cdot$$

$$\cdot [L^{(qu)}(\alpha,\beta;\vec{\partial},\Phi) + L_{\Pi}^{(ex)}(\alpha,\beta;\vec{\partial},\Phi)] \qquad (232)$$

with two functionals defined by

$$L^{(qu)}(\alpha,\beta;\vec{\partial},\Phi) \stackrel{def}{=} \cdot 1 + \alpha[-\frac{1}{6}\beta^2\vec{\partial}^2\Phi + \frac{1}{12}\beta^3(\vec{\partial}\Phi)^2]$$

$$+ \alpha^2[-\frac{1}{60}\beta^3\{\vec{\partial}^2\vec{\partial}^2\Phi\} + \frac{1}{360}\beta^4\{2\vec{\partial}^2(\vec{\partial}\Phi)^2 + 8\vec{\partial}\Phi\cdot\vec{\partial}\vec{\partial}^2\Phi$$

$$+ 5(\vec{\partial}^2\Phi)^2\} - \frac{1}{360}\beta^5\{5(\vec{\partial}\Phi)^2\vec{\partial}^2\Phi + 3\vec{\partial}\Phi\cdot\vec{\partial}(\vec{\partial}\Phi)^2\}$$

$$+ \frac{1}{288}\beta^6\{\vec{\partial}\Phi\cdot\vec{\partial}\Phi\}^2]$$

$$+ \alpha^3[\ldots\ldots\ldots] + \ldots\ldots,^{30} \qquad (233)$$

and

$$L_{\Pi}^{(ex)}(\alpha,\beta;\vec{\partial},\Phi) \stackrel{def}{=} \cdot \frac{1}{48}(\vec{r}-\Pi\vec{r})\cdot[2\beta\{12\vec{\partial}\Phi - 4\vec{\partial}\vec{\partial}\Phi\cdot(\vec{r}-\Pi\vec{r})$$

$$+ \vec{\partial}\vec{\partial}\vec{\partial}\Phi:(\vec{r}-\Pi\vec{r})(\vec{r}-\Pi\vec{r})\} + 2\beta^2\{1-2\vec{\partial}\Phi\cdot(\vec{r}-\Pi\vec{r})\}$$

$$- \{\vec{\partial}\vec{\partial}\Phi\cdot(\vec{r}-\Pi\vec{r})\} + \beta^3\vec{\partial}\Phi\{(\vec{r}-\Pi\vec{r})\cdot\vec{\partial}\Phi\}^2 + \ldots.]$$

$$+ \frac{\alpha}{24}(\vec{r}-\Pi\vec{r})\cdot[2\beta^2\vec{\partial}\vec{\partial}^2\Phi - 2\beta^3\{7\vec{\partial}\Phi\vec{\partial}^2\Phi + \vec{\partial}\vec{\partial}\Phi\cdot\vec{\partial}\Phi\}$$

$$+ \beta^4\{\vec{\partial}\Phi(\vec{\partial}\Phi)^2\} + \ldots.]$$

$$+ \alpha^2(\vec{r}-\Pi\vec{r})\cdot[\ldots\ldots\ldots] + \ldots\ldots\ldots \qquad (234)$$

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^{30}This functional is equivalent formally to that of the quasi-quantum virial coeffieicnt. See p 192 of the quoted book 34, et. al.. This formal equivalence can be proved easily. Nobody has obtained so far Eq. (234).

Let us see what does happen in Eq. (232) if we disregard the particle exchange effect, i.e. in the case of the quasi-quantum particle system. Mathematically, this implies that we neglect all terms of Eq. (232) corresponding to all elements of the symmetric group except only the identity element $\Pi = I$. We have, then from $(\vec{r}-\Pi\vec{r}) \equiv 0$ for $\Pi = I$,

$$L_{\Pi}^{(ex)} = 0, \quad L^{(qu)} \neq 0, \tag{235}$$

so that Eq. (232) takes the following simpler form:

$$D'_{\beta}(\vec{r},\vec{r}) = \frac{\exp(\beta F_{\beta})}{(4\pi\alpha\beta)^{3N/2}} \cdot \frac{\exp[-\beta\Phi(\vec{r})]}{N!} L^{(qu)}(\alpha,\beta;\vec{\sigma},\Phi) \tag{236}$$

with $L^{(qu)}$ given by Eq. (233). This is the diagonal element of the Neumann's density matrix in the quasi-quantum particle system under the assumption of the distinguishability of the individual particles. In this sense, we may call the series parts of Eq. (232) corresponding to $L^{(qu)}$ the quasi-quantum part of the diagonal element of the Neumann's density matrix, while $L_{\Pi}^{(ex)}$, the exchange-quantum part of it. We have known, thus, that the element $D_{\beta}(\vec{r},\vec{r})$ of the Neumann's density matrix is composed of two parts, i.e. the quasi-quantum and exchange-quantum parts. As shown in Eq. (234), the exchange-quantum part is negligible in the high temperature-region, but very significant in the low temperature-region.

If we assume, in some temperature-region, that

$$L_{\Pi}^{(ex)} \ll L^{(qu)}, \tag{237}$$[31]

[31] It is believed that there is no way to guess this temperature region theoretically in this kind of formalism except the comparison of the theoretical result with its experimental result.

then, the diagonal element of the Neumann's density matrix of Eq. (232) is, in this temperature region, approximated as

$$D_{\beta}^{\pm}(\vec{r},\vec{r}) \doteq \frac{\exp(\beta F_{\beta}^{\pm})}{(4\pi\alpha\beta)^{3N/2}} \cdot \frac{\exp[-\beta\Phi(\vec{r})]}{N!}$$

$$\cdot \sum_{\Pi} (\pm 1)^{\Pi} \exp[-\frac{(\vec{r}-\Pi\vec{r})^2}{4\alpha\beta}] \cdot L^{(qu)}(\alpha,\beta;\vec{\partial},\Phi), \qquad (238)$$

or

$$D_{\beta}^{\pm}(\vec{r},\vec{r}) \doteq \frac{\exp(\beta F_{\beta}^{\pm})}{(4\pi\alpha\beta)^{3N/2}} \cdot \frac{\exp[-\beta\Phi(\vec{r})-\beta U_0^{\pm}(\alpha,\beta;\vec{r})]}{N!}$$

$$\cdot L^{(qu)}(\alpha,\beta;\vec{\partial},\Phi) \qquad (239)$$

with the definition of Eq. (233), by using Eq. (227) or (229). This approximated diagonal element is different from that of Eq. (236) of the quasi-quantum particle system by only the so-called exchange effective potential $U_0^{\pm}$ appearing exponentially, within the different normalization constants of them. Since any identical particle-system is, in nature, quantum-mechanical as well as indistinguishable, it is believed that Eq. (239) is a better approximation than Eq. (236) in a realistic system.

Next, we will develop the theory of the approximation of the quantum pair-correlation function by using Eqs. (236) and (239). We start with Eq. (236), i.e. the diagonal element of the Neumann's density matrix for the quasi-quantum particle system. As we have defined already in Eq. (151), the quasi-quantum pair correlation function $g_{\beta}'(n;\vec{r}_1,\vec{r}_2)$ is given by the function generated by operating the following operator:

$$\lim_{(V,N)\to(\infty,\infty)} V^2 \int_{V^{N-2}} d\tau'$$

on the function given by Eq. (236), i.e.

$$g'_\beta(n;\vec{r}_1,\vec{r}_2) = A' \int_{V^{N-2}} d\tau'\ e^{-\beta\phi(\vec{r})}\, {}^{(qu)}_{L}(\alpha,\beta;\vec{\partial},\phi) \tag{240}$$

where A' is an operator defined by

$$A' \overset{\text{def.}}{\equiv} \lim_{(V,N)\to(\infty,\infty)} \frac{V^2 \exp(\beta F_\beta)}{N!(4\pi\alpha\beta)^{3N/2}} \quad . \tag{241}$$

Let us substitute Eq. (233) into Eq. (240) to have our further discussion for the simplification of it by using the Gauss' divergence theorem generalized in arbitrary dimensional space. We have, then,

$$\begin{aligned} g'_\beta = A' \int_{V^{N-2}} d\tau'\ e^{-\beta\phi(\vec{r})} & [1 + \alpha[-\tfrac{1}{6}\beta^2\vec{\partial}^2\phi + \tfrac{1}{12}\beta^3\vec{\partial}\phi\cdot\vec{\partial}\phi] \\ & + \alpha^2[-\tfrac{1}{60}\beta^3\,\vec{\partial}^2\vec{\partial}^2\phi + \tfrac{1}{360}\beta^4\{2\vec{\partial}^2(\vec{\partial}\phi)^2 + 8\vec{\partial}\phi\cdot\vec{\partial}\vec{\partial}^2\phi \\ & + 5(\vec{\partial}^2\phi)^2\} - \tfrac{1}{360}\beta^5\{5(\vec{\partial}\phi)^2\vec{\partial}^2 + 3\vec{\partial}\phi\cdot\vec{\partial}(\vec{\partial}\phi)^2\} \\ & + \tfrac{1}{288}\beta^6\{\vec{\partial}\phi\cdot\vec{\partial}\phi\}^2] \\ & + \alpha^3[.....] + ...] \quad . \end{aligned} \tag{242}$$

Our further simplification of Eq. (242) should be carried out <u>within the framework of the Broyle's program</u> as we have stated already in the earlier part of 3.1. To do this, let us, at first, have a preliminary consideration about a mathematical character of each term involved in

the series form inside of [ ] of Eq. (242). Suppose that we are concerned with a realistic system of which each particle is placed mutually in the field of the analytic pair potentials $\phi(|\vec{r}_\lambda - \vec{r}_\mu|)$,$(\lambda,\mu = 1,2,3,\ldots,N;\lambda\neq\mu)$ due to the other (N-1) particles. Then, the total analytic potential function $\Phi(\vec{r})$ of the system is, in accordance with the principle of superposition of potentials, given by

$$\Phi = \frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\phi(|\vec{r}_\lambda - \vec{r}_\mu|), \tag{243}$$

where

$$\phi(|\vec{r}_\lambda - \vec{r}_\mu|) = (1-\delta_{\lambda\mu})\phi(|\vec{r}_\mu - \vec{r}_\lambda|).$$

Now, let us see whether this pair character remains in the series form of Eq. (242) composed of various kinds of the derivatives of the analytic potential function $\Phi(\vec{r})$. We start with the two kinds of the derivatives given by

$$\vec{\partial}^2\Phi, \quad \vec{\partial}\Phi\cdot\vec{\partial}\Phi$$

contained in the first order part of α inside of [ ] of Eq. (242). Since the 3N-dimensional Laplacian $\vec{\partial}^2$ is, as stated in the chapter of "Introduction" abbreviated as

$$\vec{\partial}^2 = \sum_{\nu=1}^{N}\vec{\partial}_\nu^2 ,$$

We have, for $\vec{\partial}^2\Phi$,

$$\vec{\partial}^2\Phi = (\sum_{\nu=1}^{N}\vec{\partial}_\nu^2)[\frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\phi(|\vec{r}_\lambda - \vec{r}_\mu|)] = \frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\vec{\partial}_\nu^2\phi(|\vec{r}_\lambda - \vec{r}_\mu|) ,$$

which is, after a simple formal change, reduced to

$$\vec{\partial}^2\Phi = \sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\vec{\partial}_\lambda^2\phi(|\vec{r}_\lambda-\vec{r}_\mu|). \tag{244}$$

This shows us that the Laplacian operator $\vec{\partial}^2$ leaves the pair character of the total potential function $\Phi(\vec{r})$. However, this situation is different in the case of $\vec{\partial}\Phi\cdot\vec{\partial}\Phi$. The result after a formal change is as follows:

$$\vec{\partial}\Phi\cdot\vec{\partial}\Phi = \sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\vec{\partial}_\nu\phi(|\vec{r}_\lambda-\vec{r}_\nu|)\cdot\vec{\partial}_\nu\phi(|\vec{r}_\mu-\vec{r}_\nu|). \tag{245}$$

Thus, the operator $(\vec{\partial}\ )^2$ destroys the initial pair charactor of the total potential function $\Phi(\vec{r})$. From these two facts, we can investigate easily whether the remaining terms have the pair character, or not, without any further calculation. As a result, our final conclusion is as follows: There is no term of the pair character except two terms given by

$$\vec{\partial}^2\phi, \quad \vec{\partial}^2\vec{\partial}^2\phi\ ,$$

at least, up to the second order part of α in Eq. (242). This unlucky situation places us in a trap. Nevertheless, we have still fortunately a clue how to escape from this unlucky trap. Our procedure for the pair characterization of the terms with no pair character is as follows: Let us represent the coefficient functions of α, α^2, and etc. in Eq. (242) by $p_\beta^{(1)}(\vec{r})$, $p_\beta^{(2)}(\vec{r})$, and etc., i.e.

$$p_\beta^{(1)} \overset{\text{def}}{=\!=} -\frac{1}{6}\beta^2\vec{\partial}^2\Phi + \frac{1}{12}\beta^3\vec{\partial}\Phi\cdot\vec{\partial}\Phi \ ,$$

$$p_\beta^{(2)} \overset{\text{def}}{=\!=} -\frac{1}{60}\beta^3\{\vec{\partial}^2\vec{\partial}^2\Phi\} + \frac{1}{360}\beta^4\{2\vec{\partial}^2(\vec{\partial}\Phi)^2 + 8\vec{\partial}\Phi\cdot\vec{\partial}\vec{\partial}^2\Phi + 5(\vec{\partial}^2\Phi)^2\} \qquad (246)$$

$$-\frac{1}{360}\beta^5\{5(\vec{\partial}\Phi)^2\vec{\partial}^2\Phi + 3\vec{\partial}\Phi\cdot\vec{\partial}(\vec{\partial}\Phi)^2\} + \frac{1}{288}\beta^6\{\vec{\partial}\Phi\cdot\vec{\partial}\Phi\}^2 \ ,$$

etc.,

to have, also alternatively,

$$g'_\beta = A'\int_{\tau'} d\tau'\ e^{-\beta\Phi(\vec{r})}[1 + \alpha p_\beta^{(1)}(\vec{r}) + \alpha^2 p_\beta^{(2)}(\vec{r}) + \ldots] \qquad (247)$$

$$(\tau' \equiv V^{N-2}) \ .$$

We can make a change in Eq. (247) in order to eliminate some of the trouble-making cross terms destroying the pair character of the initial potential function $\Phi(\vec{r})$, i.e.

$$e^{-\beta\Phi}p_\beta^{(1)} = -\frac{\beta^2}{12}e^{-\beta\Phi}\vec{\partial}^2\Phi + \boxed{\frac{\beta}{12}\vec{\partial}^2(e^{-\beta\Phi})}, \qquad (248)$$

and, similarly,

$$e^{\beta\Phi}p_\beta^{(1)} = \boxed{-\frac{\beta^3}{144}\vec{\partial}^2(\vec{\partial}^2\Phi e^{-\beta\Phi})} + \boxed{\frac{\beta^2}{288}\vec{\partial}^2\vec{\partial}^2(e^{-\beta\Phi})}$$

$$+ e^{-\beta\Phi}[-\frac{\beta^3}{160}\vec{\partial}^2\vec{\partial}^2\Phi + \frac{\beta^4}{1440}\{3\vec{\partial}^2(\vec{\partial}^2\Phi)^2 + 2\vec{\partial}\Phi\cdot\vec{\partial}\vec{\partial}^2\Phi\}$$

$$-\frac{\beta^5}{720}\vec{\partial}\Phi\cdot\vec{\partial}(\vec{\partial}\Phi)^2] \ , \qquad (249)$$

etc..

The terms inside of the dotted rectangles $\boxed{\quad}$ in Eqs. (248) and

(249) can be simplified by carrying out the 3(N-2)-dimensional configuration integrals by using the generalized Gauss' divergence theorem. It is as follows:

$$\int_{\tau'} d\tau' \vec{\partial}^2 (e^{-\beta\Phi}) = \int_{\tau'} d\tau' (\vec{\partial}_1^2 + \partial_2^2 + \sum_{j=3}^{N} \vec{\partial}_j^2)[e^{-\beta\Phi}]$$

$$= (\vec{\partial}_1^2 + \vec{\partial}_2^2) \int_{\tau'} d\tau' \, e^{-\beta\Phi} + \sum_{j=3}^{N} \int_{\tau'} d\tau' \, \vec{\partial}_j \cdot \vec{\partial}_j (e^{-\beta\Phi})$$

which is reduced to

$$\int_{\tau'} d\tau' \vec{\partial}^2 (e^{-\beta\Phi}) = 2\nabla^2 \int_{\tau'} d\tau' \, e^{-\beta\Phi} + \sum_{j=3}^{N} \oint_{S'} dS' \vec{n}_j \cdot \vec{\partial}_j (e^{-\beta\Phi}) \tag{250}$$

by noting that we have, in the case of pair potential,

$$\nabla \equiv \vec{\partial}_1 = -\vec{\partial}_2 \, , \quad \nabla^2 \equiv \vec{\partial}_1^2 = \vec{\partial}_2^2 \, ,$$

where S' is the (3N-7)-dimensional boundary hpersurface of the 3(N-2)-dimensional domain τ', and the vector $\vec{n}_j$ is the normal unit vector to the boundary surface s of the realistic volume V corresponding to the jth particle (j≠1,2) contained in V. Actually, e.g. for j=3, we have

$$\oint_{S'} dS' \vec{n}_2 \cdot \vec{\partial}_3 = \oint_{s} ds_3 \vec{n} \cdot \vec{\partial}_3 \int_{\tau''} d\tau'' , \tag{251}$$

with

$$\tau'' \underline{\underline{\text{def}}} \cdot V^{N-3}, \quad d\tau'' \underline{\underline{\text{def}}} \cdot \prod_{j=4}^{N} d^3 \vec{r}_j , \quad \vec{n}_3 \equiv \vec{n},$$

and

$$\sum_{j=3}^{N} \oint_{S'} dS' \vec{n}_j \cdot \vec{\partial}_j (e^{-\beta\Phi}) = (N-2) \oint_{s} ds_3 \vec{n} \cdot \vec{\partial}_3 \int_{\tau''} d\tau'' \, e^{-\beta\Phi} \, . \tag{252}$$

As we will show next, this integral of Eq. (252) becomes zero, i.e.

$$J_\beta^{(0)} \stackrel{\text{def}}{=\!=} \oint_S ds_3 \vec{n}\cdot\vec{\partial}_3 \int_{\tau''} d\tau'' \; e^{-\beta\Phi} = 0. \tag{253}$$

We have, then from Eq. (250),

$$\int_\tau d\tau' \; \vec{\partial}^2 (e^{-\beta\Phi}) = 2\overline{n}^2 \int d\tau' \; e^{-\beta\Phi} \; . \tag{254}$$

The proof of Eq. (253): Let us assume that our system is contained in a cubic volume with edges of length L. The integral of the first term in the right-hand side of Eq. (250) is, in terms of the classical pair correlation function $g_\beta^{(c)}(\vec{r}_1,\vec{r}_2)$, changed into

$$\int_{\tau'} d\tau' \; e^{-\beta\Phi} = g_\beta^{(c)}(\vec{r}_1,\vec{r}_2) N! \lambda^{3N} Q_\beta N/V^2 (N-2) \quad ,$$

where $\lambda \equiv (4\pi\alpha\beta)^{\frac{1}{2}}$.

Equation (252) is, in terms of the classical 3-body correlation function $g_\beta^{(c)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)$,

$$= \oint_S ds_3 \vec{n}\cdot\vec{\partial}_3 g_\beta^{(c)}(\vec{r}_1,\vec{r}_2,\vec{r}_3) \overline{n} N! \lambda^{3N} Q_\beta N/V^2 (N-2),$$

where $\overline{n} \equiv N/V$.

We see, therefore, that

$$\{\text{Eq.}(252)\} \div \int_{\tau'} d\tau' \; e^{-\beta\Phi} = \{\overline{n} g_\beta^{(c)}(\vec{r}_1,\vec{r}_2)\} \oint_S ds_3 \vec{n}\cdot\vec{\partial}_3 g_\beta^{(c)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)$$

$$\approx \{\overline{n} g_\beta^{(c)}(\vec{r}_1,\vec{r}_2)\}\cdot(6L^2/V) = 6\overline{n} g_\beta^{(c)} L \quad ,$$

by noting $g_\beta^{(c)}(\vec{r}_1,\vec{r}_2,\vec{r}_3) \approx V^{-1}$ so that also $\vec{\partial}_3 g_\beta^{(c)}(\vec{r}_1,\vec{r}_2,\vec{r}_3) \approx V^{-1}$ as

$L \to \infty$ if $\vec{r}_3$ is on the boundary surface s and $(\vec{r}_1, \vec{r}_2)$ are fixed at two points near the center of the cubic volume V. Therefore, the second term of Eq. (250) is negligible compared with the first term of it (This succinct proof is due to Dr. A. A. Broyles, my major professor.).

Another proof is as follows: Let us suppose that the quantum fluid under consideration is contained in an isothermal solid-bath with a spherical wall of the volume $V = 4\pi R^3/3$ (R≡radius) large enough, and in its equilibrium state. Then, it is obvious that a particle on the boundary surface s of the fluid V is placed in the resultant potential field of two kinds of potentials, i.e. the internal potential Φ due to all the molecules of the fluid and the external potential Φ_o due to all the molecules of the solid-bath. Actually, these molecular forces come from only the particles contained in the two hemi-spheres of different radii (one in the fluid and another in the solid-bath) with the same center at the particle in question, which is infinitesimally very small compared with the total particles of the fluid and also of the solid-bath. Therefore, the total potential Φ' of the fluid is given by the total intermolecular potential Φ everywhere in the fluid except the vicinity of the boundary surface s. In the vicinity of the boundary surface s, the total potential Φ' is, as stated above, given by the resultant potential $\Phi + \Phi_o$, i.e.

$$\Phi' = \begin{cases} \Phi, & \text{in the region } V - \Delta V, \\ \Phi + \Phi_o, & \text{in the region } \Delta V, \end{cases} \tag{255}$$

where ΔV is the infinitesimal spherical-shell region representing the vicinity of the boundary surface s.

Now, let us consider a molecule, say, #3 molecule of the fluid come in the region ΔV by its thermal motion under the interaction with other molecules. This molecule is influenced by the force $\vec{f}_3$ given by

$$\vec{f}_3 = -\vec{\partial}_3(\Phi+\Phi_o) = (-\vec{\partial}_3\Phi) + (-\vec{\partial}_3\Phi_o) \tag{256}$$

in accordance with Eq. (255). The first term of Eq. (256) is the force due to the other molecules of the fluid, and the second term, the force due to the molecules of the bath. This force changes with time since the representative point $(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ of the fluid-system in its configuration space changes with time. The average $\vec{f}$ of the force $\vec{f}_3$ over very long time, or the statistical-mechanical average of it (≡ an ensemble average in accordance with the ergodic theorem) is, if #1 particle is fixed at the center and #2 particle, at the point $\vec{r}_2$ in the fluid sphere, given by

$$\vec{f} \equiv V^3 \int_{\tau''-\Delta\tau''}^{d\tau''} \langle\vec{r}|(-\vec{\partial}_3\Phi)e^{-\beta H}/Q_\beta|\vec{r}\rangle$$

$$+ V^3 \int_{\Delta\tau''}^{d\tau''} \langle\vec{r}|(-\vec{\partial}_3\Phi-\vec{\partial}_3\Phi_o)e^{-\beta H}/Q_\beta|\vec{r}\rangle \ , \tag{257}$$

where $\tau''-\Delta\tau'' \equiv (V-\Delta V)^{N-3}$, $\Delta\tau'' \equiv (\Delta V)^{N-3}$.

The force $\vec{f}$ is, in general, dependent upon, not only the positions $(\vec{r}_2,\vec{r}_3)$ of #2 and #3 particles, but also the temperature of the isothermal bath. However, if the radius R of the fluid-sphere is large enough compared with the distance $|\vec{r}_2|$ between #2 and #1 particles, the force $\vec{f}$ is almost independent of, not only $(\vec{r}_2,\vec{r}_3)$ but also the temperature parameter β, and it is directed along the normal unit vector $\vec{n}$ to

the boundary surface s, as long as #3 particle is in the vicinity ΔV of the sphereical boundary surface s. Furthermore, the magnitude $|\vec{f}|$ of this force must be zero since the vicinity ΔV is in statistical equilibrium with the spherical wall of the isothermal solid-bath. Therefore, Eq. (257), or the closed surface integral $\beta \oint_s ds_3 \vec{n}\cdot\vec{f}$ $(\beta \neq \infty)$ must be zero, i.e.

$$\beta \oint_s ds_3 \int_{\tau''} d\tau'' \langle \vec{r} | (-\vec{n}\cdot\vec{\partial}_3 \Phi) e^{-\beta H}/Q_\beta | \vec{r} \rangle$$

$$+ \beta \oint_s ds_3 \int_{\Delta\tau''} d\tau'' \langle \vec{r} | (-\vec{n}\cdot\vec{\partial}_3 \Phi_o) e^{-\beta H}/Q_\beta | \vec{r} \rangle = 0, \qquad (258)$$

or

$$\beta \oint_s ds_3 \int_{\tau''} d\tau'' \langle \vec{r} | (-\vec{n}\cdot\vec{\partial}_3 \Phi') e^{-\beta H}/Q_\beta | \vec{r} \rangle = 0, \qquad (259)$$

by defining again the total potential function Φ' by Eq. (255) in the vicinity of the spherical boundary surface s. Actually, the second integral term of Eq. (258) expressing the force due to the container is very small compared with the first integral term as far as the potential function Φ_o due to the molecules of the isothermal bath is not singular in the vicinity ΔV of the spherical boundary surface, since V is large enough compared with the region ΔV.

Equation (259) is, by using our formalism developed so far, reduced to

$$\beta \oint_s ds_3 \int_{\tau''} d\tau'' (-\vec{n}\cdot\vec{\partial}_3 \Phi) e^{-\beta\Phi}$$

$$\cdot \sum_{\Pi} (\pm 1)^{\Pi} \exp\left[-\frac{(\vec{r}-\vec{\Pi r})^2}{4\alpha\beta}\right] \cdot \left[L_{\Pi}^{(qu)}(\alpha,\beta;\partial,\Phi) + L_{\Pi}^{(ex)}(\alpha,\beta;\partial,\Phi)\right] = 0, \qquad (260)$$

with the definitions given by Eqs. (233) and (234). In the system of the quasi-quantum particles, Eq. (260) takes a simpler form given by

$$-\beta \oint_S ds_3 \int_{\tau''} d\tau'' \, \vec{n}\cdot\vec{\partial}_3 \Phi e^{-\beta\Phi} L^{(qu)}(\alpha,\beta;\vec{\partial},\phi) = 0 \tag{261}$$

or

$$J_\beta^{(0)} - \alpha J_\beta^{(1)} - \alpha^2 J_\beta^{(2)} - \ldots = 0, \tag{262}$$

by using Eq. (233) and defining the new integrals $J_\beta^{(\lambda)}$ (λ=1,2,3,...) by

$$J_\beta^{(\lambda)} \overset{\text{def}}{=} \beta \oint_S ds_3 \int_{\tau''} d\tau'' \, \vec{n}\cdot\vec{\partial}_3 \Phi e^{-\beta\Phi} p_\beta^{(\lambda)} \tag{262}'$$

with the definition of Eq. (246). However, it is, from Eqs. (262), (253), and (246), self-evident that the integrals $J_\beta^{(\lambda)}$ (λ=0,1,2,...) do not depend on the parameter α which is changeable in our formalism. Therefore, the sufficient and necessary condition for which Eq. (262) is valid must be that

$$J_\beta^{(\lambda)} = 0, \quad (\lambda=0,1,2,\ldots) \, . \tag{263}$$

Indeed, the correctness of the Broyles' program may be seen partly also from this proof. To put the Broyles' program on a more reliable basis, we will show alternatively below two further proofs of Eq. (259), or Eq. (253), by means of two analytical discussions. We use the quantum-mechanical cononical equation of motion given by

$$i\hbar\dot{\vec{p}}_3 = i\hbar\dot{\vec{p}}_3 = [\vec{p}_3, H] = \hbar[\vec{k}_3, H],$$

where $\vec{p}_3$, or $\vec{k}_3$ is the momentum, or wave vector operator of #3 particle corresponding to the differential operator $-i\hbar\vec{\partial}_3$, or $-i\vec{\partial}_3$. Then

Eq. (257) is written also in the following form:

$$\vec{f} = -i\frac{V^3}{Q_\beta}\int_{\tau''} d\tau'' \langle \vec{r}|[\vec{k}_3, H]e^{-\beta H}|\vec{r}\rangle \ , \tag{264}$$

with $\vec{r}_1$ (the origin) and $\vec{r}_2$ fixed in the fluid sphere, and $\vec{r}_3$ of a point on the spherical boundary surface s(exactly speaking, a point in the vicinity ΔV), where the potential operator contained in the Hamiltonian operator H is given by Eq. (255). Now, we are interested in showing analytically that the right-hand side of Eq. (264) becomes zero. Since the force $\vec{f}$ of the left-hand side of Eq. (264) does not depend upon $(\vec{r}_1, \vec{r}_2)$ if the point $\vec{r}_3$ is in the vicinity ΔV of the spherical boundary surface s ($R\to\infty$), Eq. (264) can be written in the following form independent of $(\vec{r}_1, \vec{r}_2)$:

$$\vec{f} = -i\frac{V^3}{Q_\beta}\int_{\tau''} d\tau'' \langle \vec{r}'|[\vec{k}_3, H']e^{-\beta H'}|\vec{r}'\rangle \ ,$$

where $|\vec{r}'\rangle$ is the eigenket vector of the generic position-operator, and H', the Hamiltonian operator of #3, #4, ..., #N particle-system when anyone particle is limited to be in the region ΔV. We have, then,

$$\int_s ds_3 \vec{n}\cdot\vec{f} = -i\frac{V^3}{Q_\beta}\ \underset{\Delta R\to 0}{\ell im}\ \frac{1}{\Delta R}\boxed{\int_{\Delta V} d^3\vec{r}_3 \int_{\tau''} d\tau'' \langle \vec{r}'|\vec{n}\cdot[\vec{k}_3, H']e^{-\beta H'}|\vec{r}'\rangle} \ ,$$

where ΔR is the thickness of the spherical shell ΔV. The dotted rectangular part [------] can be regarded as the trace of the operator $\vec{n}\cdot[\vec{k}_3, H']e^{-\beta H'}$ of the (N-2) particle-system, of which (N-3) particles are enclosed in the spherical box V, and one particle, in the spherical shell box $\Delta V(\equiv 4\pi R^2\Delta R)$, and it becomes zero according to the commutability

$[H', e^{-\beta H'}] = 0$ and the trace theorem $\mathrm{Tr}(Q_1Q_2Q_3) = \mathrm{Tr}(Q_2Q_3Q_1) = \mathrm{Tr}(Q_3Q_1Q_2)$. Hence, we have

$$\oint_s ds_3 \vec{n}\cdot\vec{f} = 0, \tag{265}$$

which is equivalent to Eq. (259). Since $\vec{n}\cdot\vec{f}$ is equal to $|\vec{f}|$ with a definite sign, Eq. (265) shows, in fact, that $\vec{f} = 0$.

Another proof of Eq. (253) based on classical statistical mechanics is as follows:

$$\text{Eq.(252)} \equiv \beta(N-2)\oint_s ds_3\vec{n}\cdot\boxed{\int_{\tau''} d\tau''(-\vec{\partial}_3\phi')e^{-\beta\phi'}}, \tag{266}$$

where the function Φ' represents the modified potential given by Eqs. (255). The dotted rectangular part $\boxed{\quad}$ can be expressed by

$$(Z/V^3)\vec{f}_c$$

by applying classically the same discussion as that done for obtaining Eq. (257), where Z is the classical configuration integral of the fluid system, and $\vec{f}_c$, the classical force corresponding to the quantum force $\vec{f}$ of Eq. (257). Since $\vec{n}\cdot\vec{f}_c$ does not depend upon the positions $\vec{r}_1$ (the origin), $\vec{r}_2$, and the position $\vec{r}_3$ on the spherical boundary surface s, Eq. (266) is independent of $|\vec{r}_2-\vec{r}_1| \equiv |\vec{r}_2|$, i.e. it is a thermodynamical function of the thermodynamical variables $\bar{n}$ (the density of particle number), β, and possibly the pressure p in addition to the surface tension of the fluid on its boundary surface. We have, then by using Eqs. (266), (250), (248), and (247),

$$g'_\beta(r_2) \doteqdot A'\int_{\tau'} d\tau' \exp[-\beta(\Phi' + \frac{\hbar^2\beta}{12}\vec{\partial}^2\Phi)] + 2\bar{n}^2 g_\beta^{(c)}(r_2) + C(\bar{n},\beta,p), \tag{267}$$

in the first order W.K.B.-approximation with the exponential approximation, where $C(\bar{n},\beta,p)$ is the thermodynamical function corresponding to Eq. (266). Let us put $r_2=0$ in the above equation (267) of $g'_\beta(r_2)$ to find the value of the quantity $C(\bar{n},\beta,p)$ independent of r_2. We have then by referring to the boundary condition of g'_β at $r_2=0$, i.e. $g'_\beta \to 0$ as $r_2 \to 0$,

$$0 \doteqdot 0 + 0 + C, \quad {}^{32}\therefore\ C = 0,$$

which shows us that Eq. (253) is correct, at least within the first order approximation.

Now, let us return to our main discussion. We apply the generalized Gauss' divergence theorem also to the two terms inside of the dotted rectangles [------] of Eq. (249), and neglect the surface integrals. Then, it follows that

$$\int_{\tau'} d\tau' e^{-\beta\Phi} p_\beta^{(2)} = -\frac{\beta^3}{72}\nabla^2 \int_{\tau'} d\tau' e^{-\beta\Phi}\vec{\partial}^2\Phi + \frac{\beta^2}{72}\nabla^2\nabla^2 \int_{\tau'} d\tau' e^{-\beta\Phi}$$

$$+ \int_{\tau'} d\tau' e^{-\beta\Phi}\left[-\frac{\beta^3}{160}\vec{\partial}^2\vec{\partial}^2\Phi + \frac{\beta^4}{1440}\{3\vec{\partial}^2(\vec{\partial}^2\Phi)^2 + 2\vec{\partial}\Phi\cdot\vec{\partial}\vec{\partial}^2\Phi\}\right.$$

$$\left. - \frac{\beta^5}{720}\vec{\partial}\Phi\cdot\vec{\partial}(\vec{\partial}\Phi)^2\right] . \qquad (268)$$

The substitution of Eqs. (268) and (254) into Eq. (247) gives us the

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${}^{32}\nabla^2 g_\beta^{(c)} \to 0$ as $r_2 \to 0$ comes from

$$\nabla^2 g_\beta^{(c)} = \frac{1}{x}\frac{d^2}{dx^2}(x g_\beta^{(c)}) = g_\beta^{(c)''} + 2g_\beta^{(c)'}/x, \quad (x \equiv r_2, '' \equiv d^2/dx^2),$$

by noting $g_\beta^{(c)''} \to 0$, $g_\beta^{(c)'}/x \to 0$ as $x \to 0$.

following result:

$$
\begin{aligned}
g'_\beta = A' \int_{\tau'} d\tau' e^{-\beta\phi}\Big(1 - \frac{\alpha\beta^2}{12}\vec{\partial}^2\phi\Big) \\
+ \frac{\alpha\beta}{6}\nabla^2\Big[A' \int_{\tau'} d\tau' e^{-\beta\phi}\Big(1 - \frac{\alpha\beta^2}{12}\vec{\partial}^2\phi\Big)\Big] \\
+ \frac{1}{2}\Big(\frac{\alpha\beta}{6}\Big)^2\nabla^2\nabla^2\Big[A' \int_{\tau'} d\tau' e^{-\beta\phi}\Big] \\
+ \frac{1}{2}\Big(\frac{\alpha\beta}{6}\Big)^2 A' \int_{\tau'} d\tau' e^{-\beta\phi}\Big[\boxed{- \frac{9}{20}\beta\vec{\partial}^2\vec{\partial}^2\phi} \\
+ \frac{1}{20}\beta^2\{3\vec{\partial}^2(\vec{\partial}^2\phi)^2 + 2\vec{\partial}\phi\cdot\vec{\partial}\vec{\partial}^2\phi\} - \frac{1}{10}\beta\vec{\partial}\phi\cdot\vec{\partial}(\vec{\partial}\phi)^2\Big] \\
+ \alpha^3(\ldots\ldots) + \ldots\ldots \ . \qquad (269)
\end{aligned}
$$

Next, let us combine the integral-term of the dotted rectangle $\boxed{}$ with the first integral-term in Eq. (269), and express it by a symbol $\tilde{g}_\beta$, i.e.

$$
\tilde{g}_\beta \overset{\text{def}}{=\!=} A' \int_{\tau'} d\tau' e^{-\beta\phi}\Big(1 - \frac{\alpha\beta^2}{12}\vec{\partial}^2\phi - \frac{\alpha^2\beta^3}{160}\vec{\partial}^2\vec{\partial}^2\phi\Big). \qquad (270)
$$

In the parenthesis ( ) of the second integral-term of Eq. (269), we add

$$
- \frac{\alpha^2\beta^3}{160}\vec{\partial}^2\vec{\partial}^2\phi + \boxed{\frac{\alpha^2\beta^3}{160}\vec{\partial}^2\vec{\partial}^2\phi} \ (\equiv 0), \qquad (271)
$$

while in the parenthesis ( ) of the third integral-term of Eq. (269) we add

$$
\Big(- \frac{\alpha\beta^2}{12}\vec{\partial}^2\phi - \frac{\alpha^2\beta^3}{160}\vec{\partial}^2\vec{\partial}^2\phi\Big) - \boxed{\Big(- \frac{\alpha\beta^2}{12}\vec{\partial}^2\phi - \frac{\alpha^2\beta^3}{160}\vec{\partial}^2\vec{\partial}^2\phi\Big)} \ . \qquad (272)
$$

Then, the integrals connected with the part of these two dotted

rectangles [------] of Eqs. (271) and (272) are, at most, the orders of α^3 and α^4 in their magnitudes, as long as the power series in our expansion theory is assumed to be convergent. Equation (269) is, thus, written as

$$g'_\beta = \tilde{g}_\beta + \frac{1}{1!}(\frac{\alpha\beta}{6})\nabla^2\tilde{g}_\beta + \frac{1}{2!}(\frac{\alpha\beta}{6})^2\nabla^2\nabla^2\tilde{g}_\beta + O(\alpha^2) \tag{273}$$

with the exponential approximation[33] of Eq. (270) given by

$$\tilde{g}_\beta \overset{\text{def}}{\equiv} A' \int_{\tau'} d\tau' \exp[-\beta\phi'_e(\alpha,\beta;\vec{r})], \tag{274}$$

$$\phi'_e(\alpha,\beta;\vec{r}) \overset{\text{def}}{\equiv} \phi(\vec{r}) + \frac{\alpha\beta}{12}\nabla^2\phi(\vec{r}) + \frac{\alpha^2\beta^2}{160}\nabla^2\nabla^2\phi(\vec{r}). \tag{275}$$

The operator A' contained in Eq. (274) is the normalization operator of the function g'_β defined in Eq. (247) instead of being that of the function $\tilde{g}_\beta$ itself. However, it can be, by using Eq. (273), proved easily that the normalization operators of both of these functions are equal to each other within the error of the order of α^2. In practice, the operator A' may be, therefore, regarded as the normalization operator of the function $\tilde{g}_\beta$ in our approximation theory. Equation (273) is, thus, correct up to the second term if the gradient of the total pair-potential function $\phi(\vec{r})$ (analytic) is small compared to Φ and also the higher order gradient of it becomes successively smaller in their magnitudes. The function $\tilde{g}_\beta$ defined by Eq. (274) is the classical pair correlation function with a total pair potential function $\phi'_e(\alpha,\beta;\vec{r})$ defined by Eq. (275). This potential function ϕ'_e

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[33] This approximation makes, at most, the error of the order of α^2.

is dependent upon, not only the mass of single particle, but also the temperature of the system under consideration. We call this potential $\Phi_e'(\alpha,\beta;\vec{r})$ the total quasi-quantum effective potential of the system. It is, from Eq. (275), obvious that this effective potential Φ_e' has a pair character if the original potential Φ does. Now, we are interested in finding the individual quasi-quantum effective pair potential ϕ_e' from its total potential Φ_e'. This will be done as follows:

Let $\phi_e'(|\vec{r}_\lambda-\vec{r}_\mu|)$ be this individual effective potential between $\#\lambda$ and $\#\mu$ particles in the system. We substitute Eq. (243) into Eq. (275), and then, exchange the single and double Laplacian operators with the double summation operator, according to their commutability and in order to make them operate out on the individual pair potential $\phi(|\vec{r}_\lambda-\vec{r}_\mu|)$ by noting that

$$\left[\begin{matrix}\vec{\partial}^2 & \\ \vec{\partial}^2_\nu & \vec{\partial}^2_\nu\end{matrix}\right]\phi(|\vec{r}_\lambda-\vec{r}_\mu|) = (\delta_{\nu\lambda}+\delta_{\mu\nu})\left[\begin{matrix}\vec{\partial}^2_\lambda & \\ \vec{\partial}^2_\lambda & \vec{\partial}^2_\lambda\end{matrix}\right]\phi(|\vec{r}_\lambda-\vec{r}_\mu|) \quad ,$$

and

$$\vec{\partial}^2_\lambda\phi(|\vec{r}_\lambda-\vec{r}_\mu|) = \vec{\partial}^2_\mu\phi(|\vec{r}_\lambda-\vec{r}_\mu|),$$

where the summation convention is not on the subscript λ, or μ.

We have, then,

$$\frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\phi_e'(|\vec{r}_\lambda-\vec{r}_\mu|) \overset{\text{def}}{=} \Phi_e'(\vec{r})$$

$$= \frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\phi(|\vec{r}_\lambda-\vec{r}_\mu|) + \frac{\alpha\beta}{6}\vec{\partial}^2_\lambda\phi(|\vec{r}_\lambda-\vec{r}_\mu|) + \frac{9}{10}\left(\frac{\alpha\beta}{6}\right)^2\vec{\partial}^2\vec{\partial}^2\phi(|\vec{r}_\lambda-\vec{r}_\mu|) \quad .$$

This makes us have the following universal form:

$$\phi_e'(\vec{r}) \equiv \phi(r) + (\frac{\alpha\beta}{6})\nabla^2\phi(r) + \frac{9}{10}(\frac{\alpha\beta}{6})^2\nabla^2\nabla^2\phi(r) \tag{276}$$

where r is the distance between any pair of particles and ∇^2 is a 3-dimensional Laplacian operator given, in the case of its operand being spherically symmetric, by

$$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr}), \text{ or } \frac{1}{r}\frac{d^2}{dr^2}r \tag{277}$$

This individual quasi-quantum effective pair potential function $\phi_e'(r)$ is obviously dependent upon the mass of a single particle and the temperature of the system under consideration just as its total effective potential $\Phi_e'(\vec{r})$ does.

Finally, we want to develop our approximation theory of the quantum pair correlation function $g_\beta(n;\vec{r}_1,\vec{r}_2)$ by using the approximated diagonal element of the Neumann's density matrix given by Eq. (239) under the assumption of Eq. (237). The approximated quantum pair correlation function $g_\beta^\pm$ is, by its definition, given by

$$g_\beta^\pm \doteqdot A^\pm \int_{V^{N-2}} d\tau' e^{-\beta(\Phi+U_o^\pm)} L^{(qu)}(\alpha,\beta;\vec{\sigma},\Phi) \tag{278}$$

with the exchange effective potential $U_o^\pm(\alpha,\beta,\vec{r})$ defined by Eq. (229) and the normalization operator $A^\pm$ defined by

$$A^\pm \overset{\text{def.}}{=\!=} \lim_{(V,N)\to(\infty,\infty)} V^2 \exp(\beta F_\beta^\pm)/N!(4\pi\alpha\beta)^{3N/2} \tag{279}$$

We rewrite Eq. (229) in the following explicit form:

$$e^{-\beta U_0^{\pm}} \equiv e^{-\vec{r}^2/(2q\beta)} \det\left(e^{\vec{r}_\lambda \cdot \vec{r}_\mu/(2q\beta)}\right)_{\pm}$$

$$= \begin{vmatrix} 1 & e^{-q\vec{r}_1\cdot(\vec{r}_1-\vec{r}_2)} & e^{-q\vec{r}_1\cdot(\vec{r}_1-\vec{r}_3)} & \cdots\cdots & e^{-q\vec{r}_1\cdot(\vec{r}_1-\vec{r}_N)} \\ e^{-q\vec{r}_2\cdot(\vec{r}_2-\vec{r}_1)} & 1 & e^{-q\vec{r}_2\cdot(\vec{r}_2-\vec{r}_3)} & \cdots\cdots & e^{-q\vec{r}_2\cdot(\vec{r}_2-\vec{r}_N)} \\ e^{-q\vec{r}_3\cdot(\vec{r}_3-\vec{r}_1)} & e^{-q\vec{r}_3\cdot(\vec{r}_3-\vec{r}_2)} & 1 & \cdots\cdots & e^{-q\vec{r}_3\cdot(\vec{r}_3-\vec{r}_N)} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ e^{-q\vec{r}_N\cdot(\vec{r}_N-\vec{r}_1)} & e^{-q\vec{r}_N\cdot(\vec{r}_N-\vec{r}_2)} & e^{-q\vec{r}_N\cdot(\vec{r}_N-\vec{r}_3)} & \cdots\cdots & 1 \end{vmatrix}_{\pm} \tag{280}$$

where we have put $q \overset{\text{def.}}{=} 1/(2q\beta)$ i.e. a quantity inversely proportional to the square of the thermal de Broglie's wave length of the system under consideration.

It is valuable to study thoroughly the mathematical structure of of the determinant (or permanant) of Eq. (280) in connection with our procedure of the approximation, since it is believed that other authors have not treated rigorously this determinant so far. We start, at first, to study the mathematical structure of the determinant with the later study of the permanant.

Let M be the matrix of the determinant given by Eq. (280), i.e.

$$M \overset{\text{def.}}{=} \left[\exp\left\{-q\vec{r}_\lambda \cdot (\vec{r}_\lambda - \vec{r}_\mu)\right\}\right]_{-} \tag{281}$$

$$(\lambda, \mu = 1,2,3,\ldots,N),$$

and $c_\lambda (\lambda=0,1,2,\ldots,N)$ be the expansion coefficients of the following characteristic determinant of the matrix M:

$$\det(M-yI)_{-} = \sum_{\lambda=0}^{N} c_{N-\lambda} y^{\lambda}, \quad \begin{matrix} (I \equiv \text{unit matrix}) \\ (y \equiv \text{a scalar}) \end{matrix} . \tag{282}$$

We apply here the well-known Cayley-Hamilton's theorem to this determinant. We have, then,

$$\sum_{\lambda=0}^{N} c_{N-\lambda} M^{\lambda} = 0, \tag{283}$$

and

$$\det(M)_{-} = c_N \quad , \quad {}^{(AV)} \tag{284}$$

where

$$c_o = (-1)^N . \tag{284}'$$

Let us take the traces on both sides of the Cayley-Hamilton's matrix equation given by Eq. (283). We have, then,

$$c_N = -\frac{1}{N} \sum_{\lambda=1}^{N} c_{N-\lambda} x_\lambda, \tag{285}$$

where

$$\mathrm{Tr}(M^{\lambda})_{-} = x_\lambda . \tag{286}$$

We are, now, going to construct the recurrence formula of the coefficient $c_{N-\lambda}$ in terms of the traces x_λ $(\lambda=1,2,3,\ldots,N)$. We differentiate λ times the both-hand sides of Eq. (283) with respect to the matrix M, and, then, take successively the traces on their both-hand sides. This procedure gives the following recurrence formula:

$$c_{n-\lambda} = -\frac{1}{\lambda!N}\sum_{j=\lambda+1}^{N}\frac{j!}{(j-\lambda)!}\,c_{n-j}x_{j-\lambda}, \tag{287}$$

$$(\lambda=N-1,N-2,N-3,\ldots,2,1).$$

Equation (287) can be suggested as a practical method for the computation of the characteristic determinant given by Eq. (282), and it shows us that $c_\lambda(\lambda=1,2,3,\ldots,N-1,N)$ is a rational integral function (a polynomial of many variables) having the following specific form:

$$c_\lambda \equiv c_\lambda(x_1,x_2,x_3,\ldots,x_\lambda),(\lambda=1,2,3,\ldots,N-1), \tag{288}$$

and also

$$c_N \equiv c_N(x_1,x_2,x_3,\ldots,x_N). \tag{289}$$

That is, Eq. (288) interprets c_1 as a polynomial of only one variable x_1; c_2, a polynomial of two variables (x_1,x_2); c_3, a polynomial of 3 variables (x_1,x_2,x_3), and so on. Equations (289) and (284) shows us that the determinant of the matrix M is a polynomial of the traces x_λ's of N in number given by Eq. (286). Therefore, if we can determine the polynomial of Eq. (289) by some means, then we can find the explicit function of det(M)_ from Eq. (284). This will be done as follows: We calculate, at first, some of the traces x_λ of Eq. (286) by using the concrete form of det(M)_ given by Eq. (280).

$$x_1 \equiv N,\quad x_2 \equiv \sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}(1-\delta_{\lambda\mu})e^{-q(\vec{r}_\lambda-\vec{r}_\mu)^2}+N,$$

$$x_3 \equiv \sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}(1-\delta_{\lambda\mu}\delta_{\mu\nu}\delta_{\nu\lambda})e^{-(q/2)[(\vec{r}_\lambda-\vec{r}_\mu)^2+(\vec{r}_\mu-\vec{r}_\nu)^2+(\vec{r}_\nu-\vec{r}_\lambda)^2]}+N, \tag{290}$$

$$\text{etc.,}\ (AV)$$

where $\delta_{\lambda\mu}$'s are Kronecker's δ being used frequently so far. Since x_1 represents just the total number of particles in the system under consideration as shown in Eq. (290), we expand the polynomial c_N given by Eq. (289) in the Maclaurin's power series of $(x_2, x_3, \ldots, x_N)$ with remaining the constant $x_1 \equiv N$, i.e.

$$c_N(x_1, x_2, x_3, \ldots, x_N) = \sum_{n=0}^{\infty} \frac{1}{n!} \Big(\sum_{\lambda=2}^{N} x_\lambda \frac{\partial}{\partial x_\lambda} \Big)^n c_N(x_1, 0, 0, \ldots, 0). \quad (291)$$

The determinations of the expansion coefficients of Eq. (291) can be obtained by using the specific property of c_λ's of Eq. (288) and the recurrence formula of Eq. (287).(AV) It is very tedious but straightforward. The result obtained in this way with the substitution of Eq. (290) is as follows:

$$e^{-\beta U_0} \equiv \det(M)_-$$

$$= 1 - \frac{1}{2!} \sum_{\lambda=1}^{N} \sum_{\mu=1}^{N} e^{-q(r_\lambda - r_\mu)^2} (1 - \delta_{\lambda\mu}) + \frac{1}{3!} \sum_{\lambda=1}^{N} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} (1 - \delta_{\lambda\mu}\delta_{\mu\nu}\delta_{\nu\lambda})$$

$$\cdot e^{-(q/2)[(r_\lambda - r_\mu)^2 + (r_\mu - r_\nu) + (r_\nu - r_\lambda)^2]} - \cdots\cdots .$$

This is the case of the determinant. In the permanant case, we change simply every "$-$" sign into "+" sign in the expansion expression of $\det(M)_-$. This is obvious from the definition of the permanent $(M)_+$ because there is no expansion terms canceling with each others in $\det(M)_-$. We have, thus, the following final expansion-expression of Eq. (280):

$$e^{-\beta U_0^{\pm}} \equiv 1 \pm \frac{1}{2!}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}(1-\delta_{\lambda\mu})e^{-q(\vec{r}_\lambda-\vec{r}_\mu)^2}$$

$$+\frac{1}{3!}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}(1-\delta_{\lambda\mu}\delta_{\mu\nu}\delta_{\nu\mu})e^{-(q/2)[(\vec{r}_\lambda-\vec{r}_\mu)^2+(\vec{r}_\mu-\vec{r}_\nu)+(\vec{r}_\nu-\vec{r}_\lambda)^2]}$$

$$\pm \cdots\cdots\cdots \quad . \tag{292}$$

The other terms corresponding to the following products of the traces of Eq. (286):

$$\begin{gathered} x_j(j=4,5,\ldots,N);\quad x_i x_j(i,j=2,3,\ldots,N); \\ x_i x_j x_k(i,j,k=2,3,\ldots,N);\ x_i x_j x_k x_l(i,j,k,l=2,3,\ldots,N);\ \text{etc.} \end{gathered} \tag{293}$$

are smaller than the second term of Eq. (292) as long as the quantity q, or the temperature of the system is not extremely low. Therefore, we have, in Eq. (292), the following approximation:

$$e^{-\beta U_0^{\pm}} \doteq 1 \pm \frac{1}{2!}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}(1-\delta_{\lambda\mu})e^{-(\vec{r}_\lambda-\vec{r}_\mu)^2/(2\alpha\beta)}, \tag{294}$$

which is consistent with the Broyle's program. A further approximation may be done to obtain

$$\doteq \left\{\prod_{\lambda=1}^{N}\prod_{\mu=1}^{N}\left[1 \pm (1-\delta_{\lambda\mu})e^{-(\vec{r}_\lambda-\vec{r}_\mu)^2/(2\alpha\beta)}\right]\right\}^{1/2}$$

or

$$U_0^{\pm} \doteq \frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\phi_{ex}^{\pm}(|\vec{r}_\lambda-\vec{r}_\mu|), \tag{295}$$

by putting

$$\phi_{ex}^{\pm}(r) \overset{\text{def}}{=\!=} -\frac{1}{\beta}\ln(1 \pm e^{-r^2 \div (2\alpha\beta)}), \qquad (296)$$

[35]

This approximation of Eq. (295) may be better than that of Eq. (294), since it may contain some kinds of higher order terms corresponding to Eq. (293) in it. The pair potential $\phi_{ex}^{\pm}(r)$ defined by Eq. (296) may be called the individual exchange effective pair potential in connection with the individual quasi-quantum effective pair potential $\phi_e'(r)$ of Eq. (276).

Now, let us return to our approximation of Eq. (278). We put, in Eq. (278),

$$\Phi'^{\pm} = \Phi + U_0^{\pm}, \text{ or } \Phi = \Phi'^{\pm} - U_0^{\pm}, \qquad (297)$$

and apply the same procedure as that we have used for the derivation of Eq. (273). This is done simply by using $\Phi'^{\pm}$ defined by Eq. (297) in the place of Φ in the previous derivation. We have, then,

$$g_\beta^{\pm} \div g_\beta'^{\pm} + \alpha^2 \cdot A^{\pm} \int_{V^{N-2}} d\tau' e^{-\beta\Phi} e^{-\beta U_0^{\pm}} [\{-\frac{\beta^3}{6}\vec{\partial}\Phi\cdot\vec{\partial}(U_0^{\pm}/\alpha)$$

$$+ \frac{\beta^2}{6}\vec{\partial}^2(U_0^{\pm}/\alpha) + \alpha(\frac{\beta^2}{12} - \frac{\beta^3}{6})\vec{\partial}(U_0^{\pm}/\alpha)\cdot\vec{\partial}(U_0^{\pm}/\alpha)\}$$

$$+ \alpha\{.....\} + ...], \qquad (298)$$

where the first term $g_\beta'^{\pm}$ represents the same equation as Eq. (273) with only the replacement of $\Phi'^{\pm}$ defined by Eq. (297) in place of Φ

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[35] This can be, from Eq. (294), approximated also in the following function:

$$\phi_{ex}^{\pm}(r) \overset{\text{def}}{=\!=} -\frac{2}{\beta}\ln(1 \pm \tfrac{1}{2}e^{-r^2 \div (2\alpha\beta)}).$$

in Eq. (275), and making the form $(U_0^{\pm}/\alpha)$ in the integrand of the second term integral comes from the reformation of Eq. (296) in the following form:

$$\phi_{ex}^{\pm}(r) = -\frac{2\alpha}{r^2}\underbrace{x\ell n(1 \pm e^{-x})}_{\text{--dimensionless--}}, \left(x \equiv \frac{r^2}{2\alpha\beta}\right), \tag{299}$$

in order to show, in a clear way, the behavior of the exchange effective potential $U_0^{\pm}$ over whole the domain of the integration. It is, from the property of Eq. (299), believed clearly that the second term integral of Eq. (298) is the order of α^2 in its numerical value. Therefore, the approximation $g_\beta \doteq g'^{\pm}_\beta$ in Eq. (298) is correct at least up to the term of the order of α if the previously stated assumption imposed on the total potential Φ is satisfied. Thus, we may write

$$\begin{aligned}
&g_\beta^{\pm} = \tilde{g}_\beta^{\pm} + \frac{1}{1!}\left(\frac{\alpha\beta}{6}\right)\nabla^2 \tilde{g}_\beta^{\pm} + \frac{1}{2!}\left(\frac{\alpha\beta}{6}\right)^2\nabla^2\nabla^2 \tilde{g}_\beta^{\pm} + O(\alpha^2),\\
&\text{with}\\
&\tilde{g}_\beta^{\pm} \overset{\text{def}}{\equiv} A^{\pm}\int_{\tau'} d\tau' \exp[-\beta\phi_e^{\pm}(\alpha,\beta;\vec{r})]\\
&\phi_e^{\pm}(\vec{r}) \overset{\text{def}}{\equiv} \frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}(1-\delta_{\lambda\mu})\phi_e^{\pm}(|\vec{r}_\lambda - \vec{r}_\mu|)\\
&\phi_e^{\pm}(r) \overset{\text{def}}{\equiv} \phi(r) + \frac{\alpha\beta}{6}\nabla^2\phi(r) + \frac{9}{10}\left(\frac{\alpha\beta}{6}\right)^2\nabla^2\nabla^2\phi(r)\\
&\qquad + \phi_{ex}^{\pm}(r) + \frac{\alpha\beta}{6}\nabla^2\phi_{ex}^{\pm}(r) + \frac{9}{10}\left(\frac{\alpha\beta}{6}\right)^2\nabla^2\nabla^2\phi_{ex}^{\pm}(r) \quad .
\end{aligned} \tag{300}$$

This is our final result of the approximated quantum radial distribution function $g_\beta^{\pm}$ correct, at least, up to the term of the order of α ($\equiv 5.6\times10^{-55}$/m erg cm^2). We will call hereafter the new potential

the quantum effective pair potential, which is composed of two kinds of effective pair potential, i.e the quasi-quantum and exchange effective pair potentials. For example, let us calculate the quantum effective pair potential $\phi_e^{\pm}(r)$ for the electron fluid. Since we have $\phi = e^2/r$, $\nabla^2\phi$ gives $-4\pi e^2\delta(\vec{r})$, and

$$\nabla^2\nabla^2(1/r) = -4\pi\nabla^2\delta(\vec{r}) = -4\pi\nabla^2\left[\frac{1}{(2\pi)^3}\int_{\infty} d^3k e^{-i\vec{k}\cdot\vec{r}}\right]$$

$$= (1/\pi)\int_0^{\infty} dk\, k^4 \int_0^{\infty} d\theta \sin\theta\, e^{-ikr\cos\theta},$$

which is, after the integration with respect to the variable θ, reduced to

$$= \frac{1}{2\pi ir}\int_0^{\infty}(e^{ikr}-e^{-ikr})k^3dk. \tag{301}$$

We have been confronted with a convergence difficulty in this integral. The convergence difficulty like this appears frequently also in the quantum scattering problem. Following Dirac's idea[12](1947) in the quantum scattering theory, we insert a converging factor $\exp(-\epsilon k)$, $\epsilon>0$, in Eq. (301), and modify it in the following form:

$$\nabla^2\nabla^2\left(\frac{1}{r}\right) = \frac{1}{2\pi ir}\lim_{\epsilon\to 0}\int_0^{\infty}(e^{-(\epsilon-ir)k}-e^{-(\epsilon+ir)k})k^3dk \quad .$$

The result of calculation of this integral is

$$\nabla^2\nabla^2\left(\frac{1}{r}\right) = \frac{1}{2\pi ir}\left[(4)\cdot\lim_{\epsilon\to 0}\left[\frac{1}{(\epsilon-ir)^4}-\frac{1}{(\epsilon+ir)^4}\right]\right] = 0. \tag{302}$$

Hence, the quasi-quantum effective pair potential $\phi_e'(r)$ of the electron fluid is given by

$$\phi_e'(r) = \frac{e^2}{r} - \frac{2\pi e^2\alpha\beta}{3}\delta(r) \quad . \tag{303}$$

The exchange effective pair potential is the same through every kind of particle except its microscopic characteristic constant $\alpha(\equiv\hbar^2/2m)$. we will calculate this universal form of the exchange effective pair potential in a later section.

In the next section, we will discuss the powerful method for the practical determination of the approximated quantum radial distribution function $g_\beta^\pm$ given by Eq. (300).

3.3. The Practical Determination of the Approximated Quantum Radial Distribution Function

The approximated quantum radial distribution function $g_\beta^\pm(r)$ of Eq. (300) is found by determining the function $\tilde{g}_\beta^\pm(r)$. This function $\tilde{g}_\beta^\pm(r)$ is nothing but the classical radial distribution function $g_\beta^{(c)}$ defined by

$$g_\beta^{(c)}(r) \underset{\equiv\equiv}{\text{def}} \cdot A^{(c)} \int_{\tau'} d\tau' e^{-\beta\Phi(\vec{r})}; \quad A^{(c)} \equiv (\text{the normalization operator}), \tag{304}$$

with the simple replacement of the quantum effective potential $\Phi_e^\pm(\vec{r})$ in place of the classical realistic potential $\Phi(\vec{r})$, i.e. they are mathematically equivalent to each other. Therefore, the theoretical method of determining the classical radial distribution function is applicable equally also to the case of the function $\tilde{g}_\beta^\pm(r)$. We will, thus, discuss below briefly the historical survey and recent trend of the progress in the study of the classical radial distribution function $g_\beta^{(c)}(r)$ defined by Eq. (304).

Unfortunately, the analytic determination of the exact classical radial distribution function is only possible in a one-dimensional

fluid, at least, at present stage. It is given by

$$g_{\beta}^{(c)}(x) = \frac{1}{n} e^{-\beta p x} \sum_{\lambda=1}^{\infty} [\mathcal{L}(\beta p;x) e^{-\beta \phi(x)}]^{-\lambda} \cdot \frac{1}{2\pi i} \oint_{c} dz e^{xz} [\mathcal{L}(z;x) e^{-\beta \phi(x)}]^{\lambda} \tag{305}$$

where $n \equiv$(the linear density of the particle number), $p \equiv$(the pressure of the system under consideration), and the notation of the form $\mathcal{L}(y;z)$ is the Laplace's transformation operator given by

$$\mathcal{L}(y;x) \overset{\text{def.}}{\equiv\equiv} \int_{0}^{\infty} dx e^{-yx} \quad .$$

The path c of integration in the contour integral encloses the poles of the integrand and may be calculated by means of the theory of residues.

This result of Eq. (305) was obtained first by Zernicke and Prins.[38] If we apply Eq. (305) to the simplest systems of hard spheres of diameter a, we obtain, then, the following $g^{(c)}$-function:[36]

$$g_{\beta}^{(c)}(x) = \begin{cases} 0, (x<a), \\ \sum_{\lambda=-\infty}^{m(x)} \frac{(nx-\lambda na)^{\lambda-1}}{(\lambda-1)!(1-na)^{\lambda}} e^{-n(x-\lambda a)(1-na)}, (x>a), \end{cases} \tag{306}$$

where $m(x)$ is the maximum integer among the integers m satisfying the inequality $x - ma > 0$.

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[36] We call hereafter the radial distribution function simply the g-function.

This $g^{(c)}$-function of hard spheres was obtained also by Frenkel (1945) on the consideration purely based on the mathematical theory of probability.

The general and systematic study of determining the $g^{(c)}$-function in 3-dimensional problem was given first by Kirkwood.[39,40] He introduced the so-called coupling parameter ξ in the mathematical expression of the total pair potential of the system and, then, constructed a chain of coupled integral equations. As a first approximation for the $g^{(c)}$-function, Kirkwood suggested that the triple correlation function $g_\beta^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ be factored approximately into 3 pair correlation function , i.e.

$$g_\beta^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3) \doteq g_\beta^{(c)}(\vec{r}_1,\vec{r}_2)g_\beta^{(c)}(\vec{r}_2,\vec{r}_3)g_\beta^{(c)}(\vec{r}_3,\vec{r}_1). \tag{307}$$

This is the so-called Kirkwood's principle of the superposition approximation. This principle does not originate from any statistical point of view. Therefore, it can be regarded as an assumption introduced only for the purpose of simplifying the mathematical calculation concerned with the chain of coupled integral equations, i.e. to truncate the hierarchy of the exact coupled integral equations. However, it turned out that this "ad hoc" mathematical assumption is rather qualitatively significant in connection with predicting the phenomenon of the phase transition of the system.[41] The approximate integral equation obtained under this assumption is as follows:

$$\ell n\, g_\beta^{(c)}(|\vec{r}_2-\vec{r}_1|;\xi) + \xi\beta\phi(|\vec{r}_2-\vec{r}_1|)$$
$$+ n\beta\int_0^\xi d\xi \int_\infty d^3r_3\phi(|\vec{r}_3-\vec{r}_1|)g_\beta^{(c)}(|\vec{r}_3-\vec{r}_1|;\xi)[g_\beta^{(c)}(|\vec{r}_3-\vec{r}_2|)-1] = 0. \tag{308}$$

This is called the Kirkwood's non-linear integral equation by the superposition approximation. Kirkwood and his co-worders have, later, applied this integral equation to determine the $g^{(c)}$-functions of rigid spheres and Lennard-Jones' potential[42] and his result has been confirmed to be moderately successful.[43]

On the other hand, after the presentation of the Kirkwood's theory, an infinite chain of linear integro-differential equations different from that of Kirkwood is constructed independently by Born and Green[44] and by Bogolyubov[45] by using the configuration part of the Gibbs distribution function, viz. the classical probability density function. It is as follows:

$$\vec{\partial}_1 g_\beta^{(\lambda)} + \beta g_\beta^{(\lambda)} \vec{\partial}_1 \Phi_\lambda + n\beta \int_\infty d^3\vec{r}_{\lambda+1} g_\beta^{(\lambda+1)} \vec{\partial}_1 \phi(|\vec{r}_1 - \vec{r}_{\lambda+1}|) = 0 \qquad (309)$$

$$(\lambda = 1, 2, 3, \ldots, \infty) ,$$

where e.g., $g_\beta^{(\lambda)}$ represents the correlation function of λ particles, and the function Φ_λ, the total pair potential energy of λ particles, viz.

$$\Phi_\lambda \overset{\text{def.}}{\equiv\equiv} \frac{1}{2} \sum_{j=1}^{\lambda} \sum_{i=1}^{\lambda} (1-\delta_{ij}) \phi(|\vec{r}_j - \vec{r}_i|) .$$

We call Eq. (309) the Born-Green-Bogolyubov's coupled linear integro-differential equation for the infinite chain of the exact correlation functions. Born and Green applied, furthermore, the Kirkwood's principle of the superposition approximation of Eq. (307) to this infinite chain of coupled linear integrao-differential equation of Eq. (309) to

truncate its hierarchy structure, and obtained the following non-linear integral equation:

$$\ell n\, g_\beta^{(c)}(|\vec{r}_2-\vec{r}_1|) + \beta\phi(|\vec{r}_2-\vec{r}_1|)$$

$$+ 2\pi n\beta \int_0^\infty d|\vec{r}_3-\vec{r}_1| \int_{r-|\vec{r}_3-\vec{r}_1|}^{r+|\vec{r}_3-\vec{r}_1|} d|\vec{r}_3-\vec{r}_2| \frac{d\phi(|\vec{r}_3-\vec{r}_1|)}{d|\vec{r}_3-\vec{r}_1|} g_\beta^{(c)}(|\vec{r}_3-\vec{r}_1|)[g_\beta^{(c)}(|\vec{r}_3-\vec{r}_2|)-1]$$

$$\cdot\, |\vec{r}_3-\vec{r}_2| \left\{ |\vec{r}_3-\vec{r}_1|^2 - (|\vec{r}_3-\vec{r}_2|-|\vec{r}_2-\vec{r}_1|)^2 \right\} \div \left\{ 2|\vec{r}_2-\vec{r}_1| \right\}, \qquad (310)$$

where the limit r of integration stands for $r \overset{\text{def}}{=\!=} |\vec{r}_2-\vec{r}_1|$. This non-linear integral equation was derived initially by Yvon,[46] and later independently by Born and Green.[44] Thus, Eq. (310) is called the Born-Green-Yvon integral equation. Green has succeeded in solving analytically this non-linear integral equation by introducing further assumptions somewhat complicated to analyze.[47]

These two approximate integral equations of Eqs. (308) and (310) may be written in a common form given by

$$\ell n\, g_\beta^{(c)}(r;\xi) + \beta\xi\phi(r)$$

$$+ 2\pi n\beta \int_0^\infty d|\vec{r}_2-\vec{r}_3| [K(r-|\vec{r}_3-\vec{r}_2|;\xi) - K(r+|\vec{r}_3-\vec{r}_2|;\xi)]$$

$$\cdot\, [g_\beta^{(c)}(|\vec{r}_2-\vec{r}_3|)-1]|\vec{r}_3-\vec{r}_2|/r = 0 \qquad (311)$$

$$(r \equiv |r_2-r_1|),$$

by defining each kernel $K(x;\xi)$ by

$$K(x;\xi) \overset{\text{def.}}{\equiv\equiv} \begin{cases} (\xi/2)\int_{|x|}^{\infty} dy \frac{d\phi(y)}{dy}(y^2-x^2) g_\beta^{(c)}(y), & \text{(Born-Green-Yvon)} \\ -\int_0^{\infty} d\xi \int_{|x|}^{\infty} dy \phi(y)\, g_\beta^{(c)}(y) y, & \text{(Kirkwood)} \end{cases} .$$

The approximate integral equation of Eq. (311) is to be solved subject to the boundary condition given by

$$\lim_{r\to\infty} g_\beta^{(c)}(r) = 1. \tag{312}$$

A similar integral equation but somewhat different from the Born-Green-Yvon's integral equation was obtained also by Bogolyubov by applying the Kirkwood's principle of the superposition approximation. It is as follows:[45]

$$\ell n\, g_\beta^{(c)}(r) + \beta\phi(r) + \frac{2\pi n\beta}{r}\int_0^{\infty} dr'\, r'[g_\beta^{(c)}(r')-1]\int_{|r-r'|}^{|r+r'|} dx\, x\, \textcircled{\scriptsize U}_\beta(x) = 0, \tag{313}$$

with

$$\textcircled{\scriptsize U}_\beta(x) \overset{\text{def.}}{\equiv\equiv} \int_{\infty}^{x} dy \frac{d\phi(y)}{dy}\, g_\beta^{(c)}(y) .$$

This is called the Bogolyubov's non-linear integral equation for the approximate determination of the $g^{(c)}$-function. At this point, it should be noted that the kernels themselves in Eqs. (311) and (313) depend on the unknown function of $g_\beta^{(c)}(r)$. This character is strongly different from those of the well-known Volterra and Fredholm integral equations in the theory of linear integral equations.

A comparison between the theoretical prediction based on the Kirkwood's principle of the superposition approximation[42] and the experimental data[48,49] in the realistic gaseous Argon by using the modified Lennard-Jones molecular potential, has been made right after the invention of the high-speed computer of numerical calculation. The majority of the calculations were made with Eq. (313). As a result, at low and moderate densities of particle number, the theory agrees moderately well with experiment, but as the density increases the discrepancy of disagreement between the theoretical and experimental values increases. At densities of order of the critical density, this discrepancy is supprisingly great (about 30% and then increases even more). Thus, several attempts subsequent to the recognition of this unsatisfactory discrepancy have been made to refine the Kirkwood's principle of the superposition approximation so that a better agreement between theory and experiment can be done even for dense fluids.

Kirkwood has introduced a new partial cluster expansion-integral equation for the correlation functions;[50] and obtained a set of 12 integro-differential equation for 12 unknown correlation functions, corresponding to the maximum possible number of neighbors of a spherically symmetric particle . These equations are almost exact. However, simplification is necessary for practical calculation.

Sarolea and Mayer have developed a general method of constructing approximation to the exact equation given by Eq. (309). Unfortunately, their approximation has resulted in complex and cumbersome sets of equations, even though it exceeds in accuracy the superposition approximation.[51]

Abe has revised the Kirkwood's principle of the superposition approximation given by the form of Eq. (307) in the following form:

$$g_\beta^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3) \doteq g_\beta^{(c)}(\vec{r}_1,\vec{r}_2)g_\beta^{(c)}(\vec{r}_2,\vec{r}_3)g_\beta^{(c)}(\vec{r}_3,\vec{r}_1)\chi(\vec{r}_1,\vec{r}_2,\vec{r}_3), \tag{314}$$

and presented a theory of constructing the correction function $\chi(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ in the form of an infinite power series in the density of particle number, based on the use of the so-called "irreducible" integrals in the theory of imperfect gases.[52] A little before him, Richardson sought the best function of χ, starting from a variational principle related to the requirement of minimum free energy in the system.[53] However, his best χ was a function equal to some constant depending only on temperature and volume. This is clearly unacceptible in the theory of correlation functions which we are interested in. For if χ is equal to a constant independent of coordinates $(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ in Eq. (314), the normalization condition and the asumptotic behavior of the $g_\beta^{(3)}$-function are incorrect unless χ is equal to unity.

In order to avoid these burdensome irreducible integrals in the Abe's theory, Cole and Fisher has introduced the assumption of the so-called super-superposition approximation by extending the Kirkwood's principle of the superposition approximation and the Abe's assumption. This assumption of the super-superposition approximation is as follows:

$$g_\beta^{(4)}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) \doteq [\prod_{i=1}^{4}\prod_{j=1}^{4}(1-\delta_{ij})g_\beta^{(c)}(|\vec{r}_i-\vec{r}_j|)]^{\frac{1}{2}}$$

$$\cdot \chi(\vec{r}_1,\vec{r}_2,\vec{r}_3)\chi(\vec{r}_2,\vec{r}_3,\vec{r}_4)\chi(\vec{r}_3,\vec{r}_4,\vec{r}_1)\chi(\vec{r}_4,\vec{r}_1,\vec{r}_2) \tag{315}$$

with the boundary condition of Eq. (312) and also the boundary condition given, for $|\vec{r}_i - \vec{r}_j| \to \infty$ $(i,j=1,2,3,4; i\neq j)$, by

$$X(\vec{r}_\lambda, \vec{r}_\mu, \vec{r}_\nu) \longrightarrow 1, \quad (\lambda,\mu,\nu=1,2,3,4; \lambda\neq\mu\neq\nu), \tag{316}$$

imposed on the complete symmetric function $X(r_\lambda, r_\mu, r_\nu)$, in addition to Eq. (314). They combined Eqs. (315) and (314) with the exact basic equation of Eq. (309), and obtained the following two integro-differential equations:

$$\vec{\delta}_1 \ell n\, g_\beta^{(c)}(|\vec{r}_2 - \vec{r}_1|) + \beta \vec{\delta}_1 \phi(|\vec{r}_2 - \vec{r}_1|)$$

$$+ n\beta \int_\infty d^3\vec{r}_3 \vec{\delta}_1 \phi(|\vec{r}_3 - \vec{r}_1|) g_\beta^{(c)}(|\vec{r}_3 - \vec{r}_1|) g_\beta^{(c)}(|\vec{r}_3 - \vec{r}_2|) X(\vec{r}_1, \vec{r}_2, \vec{r}_3) = 0,$$

$$\vec{\delta}_1 \ell n X(\vec{r}_1, \vec{r}_2, \vec{r}_3) + n\beta \int_\infty d^3\vec{r}_4 \vec{\delta}_1 \phi(|\vec{r}_4 - \vec{r}_1|) g_\beta^{(c)}(|\vec{r}_4 - \vec{r}_1|)$$

$$\cdot [g_\beta^{(c)}(|\vec{r}_4 - \vec{r}_2|) g_\beta^{(c)}(|\vec{r}_4 - \vec{r}_3|) X(\vec{r}_4, \vec{r}_1, \vec{r}_2) X(\vec{r}_4, \vec{r}_2, \vec{r}_3) X(\vec{r}_4, \vec{r}_3, \vec{r}_1)$$

$$- g_\beta^{(c)}(|\vec{r}_4 - \vec{r}_1|) X(\vec{r}_4, \vec{r}_1, \vec{r}_2) - g_\beta^{(c)}(|\vec{r}_4 - \vec{r}_3|) X(\vec{r}_4, \vec{r}_3, \vec{r}_1)]$$

$$= 0 \quad . \tag{317}$$

They used the series method in finding the solution to Eq. (317), and found the result given by

$$X(\vec{r}_1, \vec{r}_2, \vec{r}_3) = 1 + n \int_\infty d^3\vec{r}_4 \prod_{j=1}^{3} \left\{ e^{-\beta\phi(|\vec{r}_4 - \vec{r}_j|)} - 1 \right\} + \ldots,$$

showing that this result is the same as that obtained by Abe.[54,55] It seems, from the form of Eq. (317), that this Cole-Fisher's non-linear

simultaneous integro-differential equation is much more difficult to solve than the Kirkwood's, Born-Green-Yvon's, and Bogolyubov's integral equations. In fact, no numerical solutions to Eq. (317) have been obtained at present time. Presumably, it seems that the computation program of obtaining the numerical solution to the Cole-Fisher integro-differential equation takes too much time and effort compared with the order of the accuracy of the expected result which will be given by it. Furthermore, we have no lucid statistical-mechanical basis for this super-superposition approximation, and if the numerical solution of this approximation gives any physically unsatisfactory answer in addition to its cumbersome program of computation, then there is also a possibility that this lower order of the superposition approximation may induce the attempt of the higher order of it so that, in the long run, we are forced to fall in a final catastrophe of this problem. Because of this reason, many workers attempted other tractable approaches to this problem by giving up the idea due to Kirkwood.

Meanwhile, Percus and Yevick approached this problem with the collective coordinate technique originated by Bohm and Pines,[56] and obtained a more reliable and tractable approximate integral equation (non-linear) than those presented ever before.[57] This is the Percus-Yevick integral equation (briefly, the PY-equation) being used widely in the theory of fluid structure at present time. At a later time, Percus has derived his integral equation with his co-worker also from another point of view, viz. the method of functional differentiation.[58,59] This method of functional differentiation has been independently

developed also by Yvon before him.[60] It is believed from a theoretical point of view, that the method of functional differentiation is theoretically more basic than any other method, at least, at present time, because this method leads to the derivation of every integral equation of the $g^{(c)}$-function known so far. We will discuss briefly about this method at the end of this historical description of the approximate integral equations for the $g^{(c)}$-function, and show the concrete form of the PY equation in connection with the description of the cluster expansion method for the approximate $g^{(c)}$-function which we will discuss next.

This method was introduced originally by Ursell[61] in the hope of handling accessibly the configuration integral of the Boltzmann factor, and developed, then, by Mayer, Born, and their collaborators.[62,63] At a later time, Mayer and his coworker have applied it to the expansion of the $g^{(c)}$-function in the power series of the particle density of the system[64] with the repetition of the work by their several followers.[65-71] As a result of it, they have arrived at obtaining an integral equation with a formal convolution(Faltung) form. It is as follows:

$$G(r) = T(r) + n\int_{\infty} d^3\vec{x}\, G(|\vec{r}-\vec{x}|)T(\vec{x}), \tag{318}$$

where, in the notation of Klein and Green,[72]

$$\begin{aligned} T(r) &= g_{\beta}^{(c)}(r)\, f(r)\, e^{\beta\phi(r)} + P(r) + B(r), \\ G(r) &= S(r) + T(r) = g_{\beta}^{(c)}(r) - 1, \\ f(r) &= e^{-\beta\phi(r)} - 1, \qquad \text{(Mayer function)}, \\ r &\overset{\text{def.}}{=\!=} |\vec{r}| \overset{\text{def.}}{=\!=} |\vec{r}_2 - \vec{r}_1|, \end{aligned} \tag{319}$$

$P(r)$ = (parallel diagram term),

$B(r)$ = (bridge diagram term),

$S(r)$ = (series diagram term).

This equation is the Ornstein-Zernicke's integral equation[73] relating the direct correlation function $T(r)$ to the $g^{(c)}$-function, and it is still exact. However, Eq. (318) contains the functions $P(r)$ and $B(r)$ remaining undetermined yet in addition to the unknown $g^{(c)}$-function within it. These undetermined two functions $P(r)$ and $B(r)$ corresponding to the parallel and bridge diagrams in the Mayer cluster integral theory may, in principle, be found by some topological consideration related to the cluster integrals. Recently, several authors including those authors of the papers quoted already tried this significant work in their favorite ways. Among them, Stell, Lado, Rice and Gray have done it in an elegant and succinct manner, even though one among the two functions $P(r)$ and $B(r)$ remains still undetermined.[74-76] We can, on the basis of the discussion about Eq. (143) of the quoted dissertation (75), put

$$P(r) = g_{\beta}^{(c)}(r)e^{\beta\phi(r)} - \ell n[g_{\beta}^{(c)}(r)e^{\beta\phi(r)}] - 1. \tag{320}$$

The combination of Eqs. (320) and (319) with Eq. (318) gives a further exact integral equation given by

$$\ell n\, U(r) = \sigma(r)\{U(r)-\ell n\, U(r)-1\}$$

$$+ n\int_{\infty} d^3\vec{x}\, G(|\vec{r}-\vec{x}|)[(1+\sigma(x))\{U(x)-\ell n\, U(x)-1\} - (1-e^{-\beta\phi(x)})U(x)] \tag{321}$$

by defining

$$x \overset{\text{def}}{=\!=} |\vec{x}|, \quad \sigma(r) \overset{\text{def}}{=\!=} B(r)/P(r), \quad U(r) \overset{\text{def}}{=\!=} g^{(c)}_{\beta(r)} \, e^{\beta\phi(r)} \, . \tag{322}$$

The exact integral equation of Eq. (321) contains now only one undetermined function $\sigma(r)$ defined by the first of Eq. (322) in addition to the unknown function $U(r)$ connected with the $g^{(c)}$-function by the second of Eq. (322) for the given molecular potential $\phi(r)$ and temperature parameter β within it. The ratio $\sigma(r)$ of the bridge diagram function $B(r)$ to the parallel diagram function $P(r)$ can be known by determining only the function $B(r)$, or the series diagram function $S(r)$ by a further topological argument, or some other means, since the function $P(r)$ is determined in terms of the $g^{(c)}$-function as was shown in Eq. (320), and also the function $S(r)$ is connected with the function $B(r)$ by

$$\ln U(r) = S(r) + B(r) \tag{323}$$

[37]

with the aid of the unknown function $U(r)$.

It seems, at the present time, that several workers are going to continue studying the exact determination of the $g^{(c)}$-function for their final successful goal on the basis of the ideas of the cluster integral technique due to Ursell and Mayer, and also the collective coordinate and functional analysis techniques due to Percus, Yevick and Yvon.(77-81)

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[37] See Eq. (1.42) of the quoted dissertation (75).

Now, let us construct the approximate integral equation for the $g^{(c)}$-function under the idea somewhat different from those of our predecessors. We introduce a function $\omega(r)$ defined by

$$\omega(r) \overset{\text{def}}{=\!=} 4\sigma(r)[\sigma(r)+1] \ , \tag{324}$$

constructed by the two coefficients of the function $(U-\ell nU-1)$ in Eq. (321). Inversely, the function $\sigma(r)$ is, in terms of $\omega(r)$, represented by

$$\sigma(r) = -\frac{1}{2} \pm \frac{1}{2}\sqrt{1+\omega(r)} \tag{325}$$

with the condition given, for every value of r, by

$$\omega(r) \geqslant -1. \tag{326}$$

This follows since we must have $1 + \omega(r) \geqslant 0$ according to the real property of the function $\sigma(r)$ for every value of r. At this point, we have no longer any criteria about $\omega(r)$ of Eq. (324) as long as we have no further information of the bridge, or series diagram function $B(r)$ or $S(r)$. We set up an assumption that there exists the upper bound of the function $\omega(r)$ which is less than 1. Then, we write

$$1 > \omega(r) \geqslant -1, \text{ or } |\omega(r)| \leqq 1 \tag{327}$$

by referring to Eq. (326), so that the range of the function $(1+\omega(r))$ inside of the square root symbol of Eq. (325) is between 0 and 2. If we take the average value 1 of 0 and 2 as the approximate value of the function $1 + \omega(r)$, or $\omega(r)$ is very small in its magnitude compared with 1, Eq. (325) gives

$$\sigma(r) \doteqdot -1, \ 0. \tag{328}$$

The combination of these two approximate values of the function $\sigma(r)$ with Eq. (321) gives the following two approximate integral equations:

$$U(r) \doteqdot 1 + n\int_{\infty} d^3x G(|\vec{r}-\vec{x}|)[e^{-\beta\phi(x)}-1]U(x), \tag{329}$$

and

$$\ell n\, U(r) \doteqdot n\int_{\infty} d^3x G(|\vec{r}-\vec{x}|)[G(x)-\ell n\, U(x)] \ . \tag{330}$$

Equation (329) is the so-called Percus-Yevick integral equation which was derived originally by Percus and Yevick with the use of the collective coordinate and functional analysis techniques, and Eq. (330) is the so-called convoluted hypernetted chain integral equation which was derived originally by several workers.[65-71] We call, hereafter, this second equation briefly the CHNC-integral equation along with the PY-integral equation. Physically, the approximations of Eqs. (329) and (330) correspond to taking $B(r) + P(r) \sim 0$ and $B(r) \sim 0$ respectively.

It is, from the standpoint of the theoretical physics, very significant that every individual physical theory constructed by the individual idea and method peculiar to it must be viewed, or deduced again from a higher unified idea and method. In this sense, the recent work done by Percus and his collaborators on the basis of the functional analysis should be highly evaluated. They introduced the fundamental

idea and method of the functional analysis originally due to Volterra[82] in their unified theory of the correlation functions.[81] We present here only the central idea and method of their theory by using our notations used so far. Their most important methodology is in the elegant application of the following Taylor-Maclaurin's expansion extended to a functional F[y] of the function $y = y(r_\lambda)$:

$$F[y+\delta y] = F[y] + \sum_{j=1}^{\infty} \frac{1}{j!} \int_{\infty} \left(\prod_{\lambda=1}^{j} d^3\vec{r}_\lambda \delta y(\vec{r}_\lambda) \right) \cdot [\mathcal{U}^j F[y] / \prod_{\lambda=1}^{j} \mathcal{U} y(\vec{r}_\lambda)] \ , \quad ^{38} \tag{330}'$$

and also the following relations of functionals:

$$\mathcal{U} y(\vec{r}_\lambda) / \mathcal{U} y(\vec{r}_\mu) = \delta(\vec{r}_\lambda - \vec{r}_\mu), \quad (81) \tag{331}$$

and

$$\int d^3\vec{r}_\nu \frac{\mathcal{U} Q[y(\vec{r}_\lambda)]}{\mathcal{U} y(\vec{r}_\nu)} \cdot \frac{\mathcal{U} y(\vec{r}_\nu)}{\mathcal{U} Q[y(\vec{r}_\mu)]} = \delta(\vec{r}_\lambda - \vec{r}_\mu), \quad (81) \tag{332}$$

where the symbol "$\mathcal{U}$" represents the derivative of the functional, and Q[y] is also an arbitrary functional. A functional may be regarded as a vector in the abstract space (Banach space) with the continuous dimensions each of which corresponds to each vector in the Hilbert space. Therefore, the following operator T:

$$T \overset{\text{def}}{=\!=} \cdot \ I + \sum_{j=1}^{\infty} \frac{1}{j!} \int_{\infty} \left(\prod_{\lambda=1}^{j} d^3\vec{r}_\lambda \delta y(\vec{r}_\lambda) \right) [\mathcal{U}^j / \prod_{\lambda=1}^{j} \mathcal{U} y(\vec{r}_\lambda)] \tag{333}$$

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[38] See P 26 of the quoted book (82).

obtained from the right-hand side of Eq. (330)', is interpreted as the Taylor-Maclaurin's expansion operator in this higher abstract space than the Hilbert Space. Equation (330)' is, by the aid of this expansion operator T, written more briefly as

$$F[y+\delta y] = TF[y]. \tag{334}$$

Next, they introduced, as their mathematical trick, a very weak external potential $U(\vec{r}_\lambda)$ in addition to the internal potential energy $\Phi(\vec{r})$ of the equilibrium system under consideration, and put, in Eq. (334), or (330)',

$$\delta y(\vec{r}_\lambda) = e^{-\beta U(\vec{r}_\lambda)} - 1, \tag{335}$$

$$F[y(\vec{x})+\delta y(\vec{x})] = n'(\vec{x})e^{\beta U(\vec{x})}, \tag{336}$$

where $n'(\vec{x})$ is the density of particles at a point $\vec{x}$ in the system under the external potential $U(\vec{x})$. They have found that the functional derivative of jth order of the functional of Eq. (336) is given by the following Ursell function $\mathcal{U}_{j+1}(\vec{x},\vec{r}_1,\ldots,\vec{r}_j)$:

$$\mathcal{D}^j F[y] \Big/ \prod_{\lambda=1}^{j} i\mathcal{D}y(\vec{r}_\lambda) = \mathcal{U}_{j+1}(\vec{x},\vec{r}_1,\ldots,\vec{r}_j)$$

$$\stackrel{\text{def}}{=} n_{n+1}(\vec{x},\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_j) - \sum_{\lambda=1}^{j} \binom{j}{\lambda} \left\{ n_\lambda(\vec{x},\vec{r}_1,\ldots,\vec{r}_{\lambda-1})\, \mathcal{U}_{j+1-\lambda}(\vec{r}_\lambda,\ldots,\vec{r}_j) \right\}_{P.A.} \tag{337}$$

[39]

where $\mathcal{U}_{j+1}$ and $\mathcal{U}_{j+1-\lambda}$ are the two Ursell functions connected recursively with each other, and the notation $\{\ \}_{P.A.}$ indicates an average over

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[39] See P II 54, Eq. (4.23) of the quoted book (81).

particle permutations including the particle corresponding to the position vector $\vec{x}$, and $n_\lambda(\vec{x},\vec{r}_1,\ldots,\vec{r}_{\lambda-1})$ is the λ particle distribution function related with the λ particle correlation function $g^{(\lambda)}(\vec{x},\vec{r}_1,\ldots,\vec{r}_{\lambda-1})$ by

$$n_\lambda(\vec{x},\vec{r}_1,\ldots,\vec{r}_{\lambda-1}) = n(\vec{x})n(\vec{r}_1)\ldots n(\vec{r}_{\lambda-1})g^{(\lambda)}(\vec{x},\vec{r}_1,\ldots,\vec{r}_{\lambda-1}). \quad (338)$$

Every quantity of Eq. (338) is that of the case of no external potential U = 0, e.g. $n(\vec{x})$ is the density of particle number at the point $\vec{x}$ in the system when U = 0.

Then, Eq. (330)' takes, up to its second term, the following form:

$$n'(\vec{x})e^{\beta U(\vec{x})} = n(\vec{x}) + \int d^3\vec{r}_1 n(\vec{x})n(\vec{r}_1)G(\vec{r}_1,\vec{x}) \cdot (e^{-\beta U(\vec{r}_1)} - 1) + \ldots\ldots\ldots \quad (339)$$

by using the second of Eq. (319) and Eq. (338). The functional differential of Eq. (339) is

$$\delta\{n'(\vec{x})e^{\beta U(\vec{x})}\} = \int d^3\vec{r}_1 n(\vec{x})n(\vec{r}_1)G(\vec{r}_1,\vec{x})e^{-\beta U(\vec{r}_1)}\delta\{-\beta U(\vec{r}_1)\} \quad (340)$$

$$+ \ldots\ldots\ldots .$$

Therefore, we have

$$[\mathcal{D}n'(\vec{x})e^{\beta U(\vec{x})}/\mathcal{D}\{-\beta U(\vec{r}_1)\}]_{U=0} = n(\vec{x})n(\vec{r}_1)G(\vec{r}_1,\vec{x}),$$ [40]

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[40] See P 22 et seq. of the quoted book (82).

and hence, by using this functional differential quotient, it follows that

$$[\mathcal{U}n'(\vec{x})/\mathcal{U}\{-\beta U(\vec{r}_1)\}]_{U=0} = [\mathcal{U}\{n(\vec{x})e^{\beta U(\vec{x})}.e^{-\beta U(\vec{x})}\}/\mathcal{U}\{-\beta U(\vec{r}_1)\}]_{U=0}$$

$$= n(\vec{x})\delta(\vec{x}-\vec{r}_1) + n(\vec{x})n(\vec{r}_1)G(\vec{r}_1,\vec{x}), \qquad (341)$$

with the aid of Eq. (331). Taking into account the relationship given by Eq. (332), we try to find a function $C(\vec{x},\vec{r}_2)$ so that the functional differential quotient inverse to Eq. (341) is given by

$$[\mathcal{U}\{-\beta U(\vec{r}_2)\}/\mathcal{U}n'(\vec{x})]_{U=0} = \delta(\vec{x}-\vec{r}_2)/n(\vec{x}) - C(\vec{x},\vec{r}_2). \qquad (342)$$

We substitute Eqs. (342) and (341) into Eq. (332). This gives the following well-known Orstein-Zernicke integral equation:

$$G(\vec{r}_1,\vec{r}_2) = C(\vec{r}_1,\vec{r}_2) + \int_\infty d^3\vec{x}G(\vec{r}_1,\vec{x})C(\vec{x},\vec{r}_2)n(\vec{x}). \qquad (343)$$

If the density $n(\vec{x})$ of particle number is uniform and the particles in the system are in pair interaction, Eq. (343) takes the simpler form given by

$$G(\vec{r}) = C(\vec{r}) + n\int_\infty d^3\vec{x}G(|\vec{r}-\vec{x}|)C(\vec{x}), \qquad (344)$$

where $r \equiv |\vec{r}| \equiv |\vec{r}_2-\vec{r}_1|$.

The comparison of Eq. (344) with Eq. (318) allows us to recognize that

$$C(r) = T(r). \qquad (345)$$

Therefore, the function $C(\vec{x},\vec{r}_2)$ in Eq. (342) represents actually the direct correlation function.

Next, they developed the functional expansion theory in terms of the density of particle number in order to find the approximate form of the function $C(\vec{r}_1,\vec{r}_2)$ in terms of the $g^{(c)}$-function.[41] In this way, they could, under a unified idea and method based on the functional analysis, derived elegantly the Debye-Hückel,(83) Kirkwood-Salsburg,(84) Born-Green-Yvon, PY, and CHNC integral equations. They also tried to find an improved integral equation for the approximate $g^{(c)}$-function.

We have discussed so far the historical progress of the theory determining the $g^{(c)}$-function up to date. Unfortunately, every theory does, within it, not contain any information telling us the range of the error of the approximate $g^{(c)}$-function obtained from its suggested integral equation. This information can be given from the comparison of the numerical solution to the suggested integral equation with the experimental data, or the values calculated from the exact $g^{(c)}$-function known by some other kind of means, e.g. the Monte Carlo method.

Recently, the systematic and well-organized study of investigating the semi-analytical and numerical solutions to the Born-Green-Uvon, PY-, CHNC-integral Equations has been carried out by Broyles and his co-workers by using several potentials such as the Coulomb, Lennard-Jones 6-12, Gaussian, hard sphere potentials and others, and compared with the experimental $g^{(c)}$-functions obtained from x-ray and neutron scatterings by liquids, the numerical $g^{(c)}$-functions given by the Monte Carlo method, and also the near-exact $g^{(c)}$-functions obtained by others.(85-95) The work with the same object has been done also by

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[41] See P II 62 et seq. of the quoted book (81).

others.[96-98] Their conclusion on the basis of the solutions carried out by them is as follows: The PY- and CHNC-integral equations are much superior to the Born-Green-Yvon integral equation both at low and high densities of particles, even though the former predict that there is no phase transition phenomenon while the latter predicts it qualitatively. In the former, the PY-integral equation gives likely the better answer than the CHNC-integral equation does at high temperatures or hard sphere like potentials.

We will, in a later section, be concerned again with this problem in the case of the Ne-quantum fluid. Finally, it is worthwhile to note that the PY-integral equation has been solved exactly for hard spheres,[99,100] and the following asymptotic formula has been proved rigorously:

$$\lim_{r\to\infty} g_{\beta}^{(c)}(r) = 1 + O(N^{-\nu}), \quad \nu > 1, \qquad (101) \qquad (346)$$

where "O" is the Landau's symbol.

3.4. The Experimental Determination of the Quantum Radial Distribution Function by X-ray and Neutron Scatterings.

In this section, we discuss the relationship between the radial distribution function (quantum) and the differential cross section of the scattering of the photon (x-ray) and neutron by a fluid according to the fashion of our formalism.

The physical behaviors of the photon and neutron are, in nature, quantum-mechanical. We will construct our theory of the scattering of photon and neutron by a fluid on the basis of the Schrödinger-Heisenberg quantum mechanics.

Let us suppose that a fluid target containing one kind of N molecules in a volume V is bombarded by the beam of photons, or neutrons with the initial state $|\vec{k}\rangle$ and mass m_s, and changes the initial state of the bombarding particle into the final state $|\vec{k}_s\rangle$ after the scattering process is taken place by the interaction H' between them. Let $|i\rangle$ and $|f\rangle$ be the initial and final states of the fluid target before and after the scattering event respectively. Then, the inelastic differential scattering cross section $d^2\sigma(i\to f)/d\Omega\, d\omega$ per unit solid angle per unit energy (in the unit of $\hbar$) is given by

$$\frac{d^2\sigma(i\to f)}{d\Omega\, d\omega} \doteq V\left(\frac{2\pi\sqrt{m_s}}{\hbar}\right)^4 \frac{k_s}{k} \left|\langle f|\langle \vec{k}_s|H'|\vec{k}\rangle|i\rangle\right|^2$$

$$\cdot\delta(\omega-\omega_i+\omega_f), \qquad (347)$$

in the first order approximation (Born's) as well known in the quantum-mechanical theory of the scattering process,[42],(102) where ω_i and ω_f are the total energies in the unit of $\hbar$, i.e. $\omega_i \equiv E_i/\hbar$, $\omega_f \equiv E_f/\hbar$ at the initial and final states of the fluid target respectively, and ω, a variable representing an energy value in this unit.

Now, we assume the pair character of the interaction H' between the bombarding particle and the bombarded N particles of the fluid target with the neglection of their spin-spin interaction, viz.

$$H' = \sum_{\lambda=1}^{N} \phi'(|\vec{x}-\vec{r}_\lambda|), \qquad (348)$$

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[42] See Eq. (15), P 193 of the quoted book (12).

where $\vec{x}$ is the position vector of the bombarding particle, and $\vec{r}_\lambda$ (λ=1,2, 3,...,N), the position vector of the N particles of the fluid target respectively. We have, then,

$$\langle \vec{k}_s | H' | \vec{k} \rangle = \sum_{\lambda=1}^{N} \langle \vec{k}_s | \phi'(| \vec{x} - \vec{r}_\lambda |) | \vec{k} \rangle \ .$$

We put the identity operator I given by

$$I = \int_\infty d^3\vec{x} | \vec{x} \rangle \langle \vec{x} |$$

between the bra vector $\langle \vec{k}_s |$ and the individual interaction operator $\phi'(| \vec{x} - \vec{r}_\lambda |)$, to see that

$$= \frac{1}{(2\pi)^3} \sum_{\lambda=1}^{N} \int_\infty d^3\vec{x} \phi'(| \vec{x} - \vec{r}_\lambda |) e^{-i(\vec{k}_s - \vec{k}) \cdot \vec{x}},$$

or

$$\langle \vec{k}_s | H' | \vec{k} \rangle = \frac{1}{(2\pi)^3} \sum_{\lambda=1}^{N} \tilde{\phi}'(k') e^{-i\vec{k}' \cdot \vec{r}_\lambda} \qquad (3\text{-}9)$$

by putting

$$\vec{k}' \stackrel{def}{=\!=} \vec{k}_s - \vec{k}, \quad k' \stackrel{def}{=\!=} | \vec{k}' |, \quad \tilde{\phi}'(k') \stackrel{def}{=\!=} \int_\infty d^3\vec{x} \phi'(x) e^{-i\vec{k}' \cdot \vec{x}} \ .$$

We note here that $\tilde{\phi}'(k')$ is the Fourier transform of the individual interaction $\phi'(| \vec{x} |)$.

Next, let us suppose that we perform the measurement of the total energy of the fluid target before and after the scattering process

is taken place and finished. Then, we will find correspondingly two energy eigenvalues $E_{\vec{n}}$ and $E_{\vec{n}'}$ of the eigenstates $|\vec{n}\rangle$ and $|\vec{n}'\rangle$ of the quantum-mechanical system of fluid target respectively. For this process of transition $\vec{n} \rightarrow \vec{n}'$, Eq. (347) is, with the aid of Eq. (349), and $|i\rangle = |\vec{n}\rangle$ and $|f\rangle = |\vec{n}'\rangle$, written in the following form:

$$\frac{d^2\sigma(\vec{n}\rightarrow\vec{n}')}{d\Omega\, d\omega} \doteq V\left(\frac{m_s}{2\pi\hbar^2}\right)^2 \cdot \frac{k_s}{k} \cdot |\tilde{\phi}'(k')|^2 \cdot \delta(\omega-\omega_{\vec{n}}+\omega_{\vec{n}'})$$

$$\cdot \sum_{\lambda,\mu=1}^{N} \langle\vec{n}|e^{-i\vec{k}'\cdot\vec{r}_\lambda}|\vec{n}'\rangle\langle\vec{n}'|e^{+i\vec{k}'\cdot\vec{r}_\mu}|\vec{n}\rangle, \qquad (350)$$

where $\omega_{\vec{n}} \equiv E_{\vec{n}}/\hbar$, $\omega_{\vec{n}'} \equiv E_{\vec{n}'}/\hbar$.

Now, let us suppose that this scattering process has been carried out with the fluid target contact with the big isothermal bath of the temperature parameter β. Then, the probability of finding this fluid target at its eigenstate $|\vec{n}\rangle$ is, as we have discussed already in the section 2.2 on the basis of our formalism, given by

$$|\langle\vec{n}|\beta\rangle|^2 .$$

Therefore, Eq. (350) is, in this case, written as

$$\frac{d^2\sigma_\beta}{d\Omega\, d\omega} \doteq V\left(\frac{m_s}{2\pi\hbar^2}\right)^2 \cdot \frac{k_s}{k} \cdot |\tilde{\phi}'(k')|^2 \sum_{\vec{n}'} \sum_{\vec{n}} |\langle\vec{n}|\beta\rangle|^2$$

$$\cdot \delta(\omega-\omega_{\vec{n}}+\omega_{\vec{n}'}) \cdot \sum_{\lambda,\mu=1}^{N} \langle\vec{n}|e^{-i\vec{k}'\cdot\vec{r}_\lambda}|\vec{n}'\rangle\langle\vec{n}'|e^{i\vec{k}'\cdot\vec{r}_\mu}|\vec{n}\rangle, \qquad (351)$$

where the summation $\sum_{\vec{n}'}$ comes from the use of the addition theorem of probability for all possible final states $|\vec{n}'\rangle$'s.

Now, we are going to change Eq. (351) into its alternative form by using the integral form of the δ-function $\delta(\omega-\omega_{\vec{n}}+\omega_{\vec{n}'})$ given by

$$\delta(\omega-\omega_{\vec{n}}+\omega_{\vec{n}'}) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\ e^{i(\omega-\omega_{\vec{n}}+\omega_{\vec{n}'})t} \quad .$$

Then, the expression inside of the dotted rectangle [ ] in Eq. (351) is changed into

$$= \frac{1}{2\pi}\sum_{\lambda,\mu=1}^{N}\int_{-\infty}^{\infty} dt\ e^{i\omega t}\langle\vec{n}|e^{-i\vec{k}'\cdot\vec{r}_\lambda}|\vec{n}'\rangle e^{i\omega_{\vec{n}'}t}\langle\vec{n}'|e^{i\vec{k}'\cdot\vec{r}_\mu}|\vec{n}\rangle e^{-i\omega_{\vec{n}}t},$$

or

$$= \frac{1}{2\pi}\sum_{\lambda,\mu=1}^{N}\int_{-\infty}^{\infty} dt\ e^{i\omega t}\langle\vec{n}|e^{-i\vec{k}'\cdot\vec{r}_\lambda}|\vec{n}'\rangle\langle\vec{n}'|e^{i\vec{k}'\cdot\vec{r}_\mu(t)}|\vec{n}\rangle \qquad (352)$$

by noting that

$$e^{i\omega_{\vec{n}'}t}\langle\vec{n}'| = \langle\vec{n}'|e^{iHt/\hbar}\ ;\ |\vec{n}\rangle e^{-i\omega_{\vec{n}}t} = e^{-iHt/\hbar}|\vec{n}\rangle\ ,$$

and defining the following operator in the Heisenberg picture:

$$e^{i\vec{k}'\cdot\vec{r}_\mu(t)} \underline{\underline{\text{def}}} \cdot e^{iHt/\hbar}e^{i\vec{k}\cdot\vec{r}_\mu}e^{-iHt/\hbar}\ , \qquad (353)$$

where H is the Hamiltonian operator of the fluid target.

We substitute Eq. (352) into Eq. (351) to obtain

$$\frac{d^2\sigma_\beta}{d\Omega d\omega} \doteq \frac{V}{2\pi}\left(\frac{m_s}{2\pi\hbar^2}\right)^2 \cdot \frac{k_s}{k}\cdot|\vec{\mathcal{G}}'(k')|^2 \cdot \sum_{\lambda,\mu=1}^{N}\int_{-\infty}^{\infty} dt\ e^{i\omega t}$$

$$\cdot \int_{V^N} d^{3N}\vec{r}\,\langle\vec{r}|e^{i\vec{k}'\cdot\vec{r}_\mu(t)}\Big[\sum_{\vec{n}}|\vec{n}\rangle|\langle\vec{n}|\beta\rangle|^2\langle\vec{n}|\Big]e^{-i\vec{k}\cdot\vec{r}_\lambda}|\vec{r}\rangle \qquad (354)$$

by noting that

$$\sum_{\vec{n}'} |\vec{n}'\rangle\langle\vec{n}'| \equiv \mathrm{I}\ (\text{identity})$$

and inserting, instead, another form of the identity given by

$$\mathrm{I} \equiv \int_{V^N} d^{3N}\vec{r}\,|\vec{r}\rangle\langle\vec{r}| \quad .$$

The operator inside of the dotted rectangle [------] in Eq. (354) is the Neumann's density operator D_β discussed already in the section 2.2. We can, therefore, write Eq. (354) also in the following form:

$$\frac{d^2\sigma_\beta}{d\Omega d\omega} \doteq \frac{V}{2\pi}\left(\frac{m_s}{2\pi\hbar^2}\right)^2 \cdot \frac{k_s}{k} \cdot |\tilde{\phi}'(k')|^2$$

$$\cdot \sum_{\lambda,\mu=1}^{N} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \int_{V^N} d^{3N}\vec{r}\langle\vec{r}|D_\beta\, e^{-i\vec{k}'\cdot(\vec{r}_\lambda - \vec{r}_\mu(t))}|\vec{r}\rangle \quad . \qquad (355)$$

This is a useful formula containing the dynamic structure factor $\rho(\omega,\vec{k}')$ of the fluid target defined by

$$\rho(\omega,\vec{k}') \overset{\text{def}}{=\!=} \frac{1}{2\pi} \sum_{\lambda,\mu=1}^{N} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \int_{V^N} d^{3N}\vec{r}\langle\vec{r}|D_\beta\, e^{-i\vec{k}'\cdot(\vec{r}_\lambda - \vec{r}_\mu(t))}|\vec{r}\rangle, \quad (356)$$

which has been derived first by Van Hove in 1954 on the basis of his formulation different from ours.[103] Now, we have to go ahead more for our final goal. The differential scattering cross section $d\sigma_\beta/d\Omega$ per unit solid angle over the whole energy range $(-\infty,\infty)$ of ω is obtained by integrating the Van Hove's dynamical structure factor $\rho(\omega,\vec{k}')$ with

respect to ω from $-\infty$ to ∞. We have, thus,

$$\int_{-\infty}^{\infty} d\omega \rho(\omega, k') = \sum_{\lambda,\mu=1}^{N} \int_{V^N} d^{3N}\vec{r} \langle \vec{r}|D_\beta \, e^{-i\vec{k}'\cdot(\vec{r}_\lambda - \vec{r}_\mu)}|\vec{r}\rangle, \tag{357}$$

by noting that

$$\int_{-\infty}^{\infty} d\omega e^{i\omega t} = 2\pi\delta(t),$$

and referring again to the Heisenberg operator of Eq. (353) at $t = 0$. The integration of Eq. (355) with respect to ω from $-\infty$ to ∞ on referring to Eq. (357) leads to the following result:

$$\frac{d\sigma_\beta}{d\Omega} \doteq V\left(\frac{m_s}{2\pi\hbar^2}\right)^2 \cdot \frac{k_s}{k} \cdot |\tilde{\phi}'(k')|^2 \cdot \sum_{\lambda,\mu=1}^{N} \int_{V^N} d^{3N}\vec{r} \langle \vec{r}|D_\beta \, e^{-i\vec{k}'\cdot(\vec{r}_\lambda - \vec{r}_\mu)}|\vec{r}\rangle. \tag{358}$$

This is the fundamental approximate equation in our theory of the scattering of photon (x-rays) and neutron by a fluid in a thermodynamical equilibrium. We may develop a theory about the creation and annihilation of photons produced by the energy transfer between the fluid target and the bombarding particles under the thermodynamical equilibrium on the basis of Eqs. (355) and (358). However, we are, in this section, concerned with only the theory of discussing the relationship between the quantum radial distribution function of the fluid target and the scattering intensity of the bombarding particle beam. For this purpose, we are going to make Eq. (358) reduce to a more concrete form to be understood easily and usefully in practice.

We simplify the summation and integral part of the dotted rectangle of Eq. (358) by introducing the quantum radial distribution function $g_\beta(x)$. Since we can write

$$\sum_{\lambda,\mu=1}^{N} e^{-i\vec{k}'\cdot(\vec{r}_\lambda-\vec{r}_\mu)} = N + \sum_{\lambda,\mu=1}^{N} (1-\delta_{\lambda\mu})e^{-i\vec{k}'\cdot(\vec{r}_\lambda-\vec{r}_\mu)},$$

this dotted rectangle part reduces to

$$= N \int_{V^N} d^{3N}\vec{r}\langle\vec{r}|D_\beta|\vec{r}\rangle + N^2 \int_{V^N} d^{3N}\vec{r}\langle\vec{r}|D_\beta|\vec{r}\rangle e^{-i\vec{k}'\cdot(\vec{r}_2-\vec{r}_1)},$$

or

$$= N + N(\frac{N}{V}) \int_V d^3\vec{x}\; g_\beta(x)e^{-i\vec{k}'\cdot\vec{x}} \quad , \tag{359}$$

by using the normalizable character of the Neumann's density operator D_β and the definition of the quantum radial distribution function $g_\beta(x)$ and putting $\vec{x} = \vec{r}_2-\vec{r}_1$.

The substitution of Eq. (359) into Eq. (358) gives us

$$\frac{d\sigma_\beta}{d\Omega} \doteq NV\cdot(\frac{m_s}{2\pi\hbar^2})^2 \cdot \frac{k_s}{k} \cdot |\vec{\phi}'(k')|^2 \cdot \left\{1 + n\int_V d^3\vec{x} g_\beta(x)e^{-i\vec{k}'\cdot\vec{x}}\right\}, \tag{360}$$

where n is the density of particle number of the fluid defined by $n \overset{def}{=\!=} N/V$.

This is the relationship between the quantum radial distribution function and the scattering intensity of the photons (x-rays) and neutrons in both cases of the elastic and inelastic scatterings. It is noticeable that the differential scattering cross section is connected

closely with the Fourier transform of the quantum radial distribution function. The result of Eq. (360) is formally in agreement with that obtained on the basis of the classical theory of the Rayleigh's scattering of the electromagnetic waves by a fluid.[76,35]

In the case of the elastic, or quasi-elastic scattering , Eq. (360) takes a simpler form. Let Θ be the angle between the scattering direction $\vec{k}_s$ and the incident direction $\vec{k}$ of the bombarding particles. Then, we have, by noting $k = k_s$ in the elastic scattering,

$$k' = |\vec{k}_s - \vec{k}| = 2k \sin\frac{\Theta}{2} = \frac{4\pi}{\lambda}\sin(\theta/2), \tag{361}$$

where λ is the de Broglie Wave length of the incident particle. The angular integral appears in the volume integral of Eq. (360) if we use the spherical coordinate system with the origin at the center of the drop of the fluid target, and it can be calculated easily. Thus, Eq. (360) is reduced to the following simpler form:

$$\frac{d\sigma_\beta}{d\Omega} \doteqdot NV \cdot \left(\frac{m_s}{2\pi\hbar^2}\right)^2 \cdot |\tilde{\phi}'(k')|^2 \cdot \left[1 + \frac{4\pi n}{k'}\int_0^{x_o} dx\, g_\beta(x) x \sin k'x\right], \tag{362}$$

where x_o is the radius of the drop of the fluid target and it may be regarded practically as $x_o \sim \infty$.

If we exclude the following differential scattering cross section due to the geometry of the surface of the fluid drop:

$$NV \cdot \left(\frac{m_s}{2\pi\hbar^2}\right)^2 \cdot |\tilde{\phi}'(k')|^2 \cdot \frac{4\pi n}{k'}\int_0^{x_o} dx\, x \sin k'x \tag{363}$$

from the differential scattering cross section of Eq. (362), we have, then,

$$\frac{d\sigma_\beta'}{d\Omega} \doteq NV \cdot \left(\frac{m_s}{2\pi\hbar^2}\right)^2 \cdot |\tilde{\phi}'(k')|^2$$

$$\cdot \left[1 + \frac{4\pi n}{k'} \int_0^\infty dx\left\{g_\beta(x)-1\right\} x \sin k'x\right], \qquad (364)$$

where we have taken $x_o = \infty$, and σ_β' is the total cross section other than that due to Eq. (363). The differential scattering cross section due to Eq. (363), i.e. the geometrical effect of the surface of the fluid drop is largely responsible for the contribution to the diffraction pattern resulting from the incident particles striking the surface of the fluid drop.[104] The first term of Eq. (364) represents the differential scattering cross section due to the scattering of the incident particles by the individual molecules of the fluid drop without any interference, i.e. the independent molecular-contribution to the scattering, in which the individual contribution due to each molecule is given by

$$V \cdot \left(\frac{m_s}{2\pi\hbar^2}\right)^2 \cdot |\tilde{\phi}'(k')|^2 . \qquad (365)$$

The total contribution, i.e. the algebraic sum of Eq. (365) over whole N molecules of the fluid drop brings the first term of Eq. (364). The second term of Eq. (364) represents the differential scattering cross section due to the scattering of the incident particles by virtue of the microscopic inhomogeneous structure of the fluid drop. The approximation $x_o \sim \infty$ in the upper limit of the integral of this part introduces

almost no error since we have, in the realistic case, almost $g_\beta(x)-1 \cong 0$ in the interval $x > r_o$ for an infinitesimally small distance r_o compared with the macroscopic radius x_o of the fluid drop. Equation (364) is the fundamental equation for the experimental evaluation of the quantum radial distribution function.

Let us represent Eq. (364) in terms of the scattering intensity $I_\beta(n,k')$ and the incident intensity I_o of the beam of the bombarding particles. This is done simply by putting, in Eq. (364),

$$d\sigma'_\beta/d\Omega = I_\beta(n,k')/I_o.$$

We have, thus,

$$I_\beta(n,k')/I(n,k') = 1 + (4\pi n/k')\int_0^\infty dx\{g_\beta(x)-1\}x \sin k'x, \qquad (366)$$

where we have defined

$$I(n,k') \stackrel{\text{def}}{=} nI_o V(m_s/2\pi\hbar^2)^2 |\tilde{\phi}'(k')|^2 . \qquad (367)$$

The quantity $I(n,k')$ defined by Eq. (367) does not depend upon the temperature of the fluid drop, and can be calculated analytically by knowing the incident intensity I_o and mass m_s of the bombarding particle, the macroscopic volume V and the particle density n of the fluid drop and the pair interaction potential between the single bombarding particle and molecule of the fluid drop. Even if the pair interaction potential is not known in advance, the quantity $I(n,k')$ can be known by the experimental measurement of the scattering intensity $I_\beta(n,k')$. The method

is as follows: Suppose that the fluid target is rarefied so that the particle density n may be regarded almost as zero, and then bombarded by the bombarding particle with the same incident energy as that to be used for the further experiment with the change in the particle density n. Then, in this experiment, the integral term of Eq. (366) may be neglected so that we have, in practice, $I = I_\beta$, or from Eq. (367),

$$\left|\tilde{\phi}'(k')\right|^2 = \lim_{n\to 0} I_\beta/nI_o V^2 \cdot (m_s/2\pi\hbar^2)^2, \tag{368}$$

i.e. the pair interaction potential can be determined experimentally by performing the measurement of I_β for the rarefied fluid. This measured intensity I_β should not depend on the temperature of the rarefied fluid, since the left-hand side and the denominator of the right-hand side of Eq. (368) involve only the quantities independent of the temperature. Thus, in principle, the left-hand side of Eq. (366) can be determined experimentally. This experimental measurement makes us evaluate the quantum radial distribution function in accordance with the inverse Fourier transform of Eq. (366) given by

$$g_\beta(x) = 1 + \frac{1}{2\pi^2 nx}\int_0^\infty \left(\frac{I_\beta(n,k')}{I(n,k')} - 1\right)k'\sin(k'x)dk'. \tag{369}$$

In the above discussion, we never have been concerned with any intrinsic character peculiar to the bombarding photon, or neutron. We have been concerned with only the mass m_s and the incident energy $\hbar^2k^2/2m_s$ which every kind of the bombarding particle possesses. Therefore, our above theory is, in principle, applicable for any kind of a bombarding particle even though the experimental difficulty may be arisen for some kind of bombarding particle. Then, Eq. (368), or Eq. (366) suggests an

experimental principle determining an intermolecular potential of a fluid. The principle is as follows: Let us suppose a scattering experiment in which the beam of a bombarding particles attacks a dense, or rarefied fluid target composed of the same kind of particles as the bombarding particles. Then, the Fourier transform $\tilde{\phi}'(k')$ contained in Eq. (368), or Eq. (366) represents actually that of the intermolecular potential of the fluid. If we measure the scattering intensity $I_{\beta}(n,k')$ in this experiment, we can, then, determine the Fourier transform $\phi'(k')$ of the intermolecular potential of the fluid target by referring to Eq. (368), or Eqs. (366) and (369). This principle of the experimental determination of the intermolecular potential of a fluid is comparable with the principle suggested on the basis of the PY-, CHNC-integral equations.[105,107]

The scattering theory discussed so far was based on the Born's approximation of the first order. We can develop the theory of the second order approximation to improve the experimental evaluation of the quantum radial distribution function. However, it has been shown in several cases of fluids that Eq. (369) gives the result in good agreement with that of the numerical calculation based on the PY-, or CHNC-integral equation.

3.5. The Numerical Calculation of the Quantum Radial Distribution Function of the Neon Fluid

We will, in this section, develop the preparatory discussion about the numerical calculation of the approximate quantum radial distribution function of the neon quantum-fluid in order to testify how much our approximation theory studied so far is correct. Before we go into this main subject, it is helpful for our later discussions to

have a brief survey of the molecular structure and several properties of the neon element to refresh our memory of the knowledge of it.

The neon atom with 10 electrons (so that the atomic number is 10) belonging to the noble (rare) element of the monoatomic molecule has 7 isotopes of the mass numbers 18, 19, 20, 21, 22, 23 and 24. Among them, the isotope 20 is most abundant with the abundance 90.8 per cent, and the next is the isotope 22 with the much less abundance 8.9 per cent followed by the isotope 21 with the quite small abundance 0.26 per cent and others totally with the faint abundance 0.04 per cent.

The 10 electrons of this neon atom are tightly bound to the nucleous with the electron configuration $1s^2\ 2s^2\ 2p^6$ occupying completely up to the spherically symmetric L-shell, of which the energy level is separated by a sizable gap from the next M-shell, thus discouraging any transformation of this atom to a non-symmetrical form which could enter into the valence relationship with other atoms. Therefore, this noble element is monoatomic and chemically inert. The monoatomic molecular weight W for this isotopic mixture is, thus, given by

$$W = 20.183.^{(108,109)} \tag{370}$$

The ore containing the neon element has not been found in the natural world until present time, but it is contained in the atmosphere with the quite small weight-percentage 0.0012 (volume-percentage 0.0018). The monoatomic molecules of neon are together at the gas state with colorlessness and odourlessness at the thermo-dynamical standard state. The two characteristic specific heats are $C_v \doteqdot 0.1476$ cal. deg.$^{-1}$ g^{-1} and $C_p \doteqdot 0.2458$ cal. deg.$^{-1}$ g^{-1}, and the thermal conductivity is

$K \doteq 1.085 \times 10^{-4}$ cal. Cm^{-1}. sec^{-1}. deg^{-1} at $0^{\circ}C$. The magnetic susceptibility is $\chi \doteq -3.9 \times 10^{-10}$ e.m.u., and the solubility is 15 cc/100cc H_2O at $20^{\circ}C$. The line spectrum of the neon atom is in the red region, and it makes very easily the electric discharge in the Geisler's tube even not at so low pressure compared with other gases.

The critical temperature T_c and pressure P_c are

$$T_c \doteq 44.48^{\circ}K, \quad P_c \doteq 26.86 \text{ atm.} \tag{371}$$

The neon liquid has the density 1.20 g/cm^3 at $27.2^{\circ}K$, and 0.9002 g/cm^3 at the vicinity of the boiling point $27.28^{\circ}K$.

The neon solid has the crystal structure of the face centered cubic with the lattice constant $a = 4.52$ Å at $20.2^{\circ}K$.

Next, we will discuss the intermolecular potential $\phi(r)$ between two monoatomic molecules of neon element, and calculate the quantum effective potential, i.e. the quasi-quantum and exchange effective potentials. As stated previously, the atoms of the neon element never have the valence relationship with other atoms.. This fact implies quantum-mechanically that there is, at least, no bound state in the system of two neon-atoms, in other words, there does not exist a negative energy eigenvalue c such that

$$[\vec{p}^2/m + \phi(|\vec{r}|)]\,|c\rangle = c\,|c\rangle\ , \tag{372}$$

where $(\vec{r},\vec{p})$ is the position operator of one neon atom relative to the other in its μ-space, and we have introduced the reduced mass $m/2$ of the two neon-atom system. Mathematically, this is interpreted as that the intermolecular potential of the neon element must, at least, be

such a function $\phi(r)$ that

$$\langle\Psi|\phi(|\vec{r}|)|\Psi\rangle \geq -\frac{1}{m}\langle\Psi|\vec{p}^2|\Psi\rangle \tag{373}$$

for all vectors $|\Psi\rangle$ in the Hilbert space.

Presumably, there would be many functions $\phi(r)$ satisfying the requirement of Eq. (373). Among them, we must choose the function $\phi(r)$ such that it can describe most accurately all the properties of the three states, i.e. gas, liquid and solid states of the neon element. Several kinds of functions with parameters but the different numerical values of the parameters even in the same kind of function have been suggested for the intermolecular potential $\phi(r)$ of the neon element up to date.[35] The most probable one among them would be the Lennard-Jones n-6 potential $\phi^{(L)}(r)$ given by the following form:

$$\phi^{(L)}(r) = \frac{n\epsilon}{n-6}\left(\frac{n}{6}\right)^{6/(n-6)}\left[\left(\frac{a}{r}\right)^n - \left(\frac{a}{r}\right)^6\right], \quad n > 6, \tag{374}$$

where (n,ϵ,a) are the three characteristic parameters. The inverse attractive potential of the second term comes from the quantum-mechanical origin. The succinct description of this origin may be seen in many standard textbooks and papers.[110,111] The inverse repulsive potential of the first term with the short range of action is chosen only for the reason of convenience to make it match with the fact that two molecules are repulsive with each other within some distance of them. Therefore, this repulsive term would represent the measure of hardness of the molecule. The depth of this potential is given simply by the value of the parameter ϵ (at $r = a(n/6)^{1/(n-6)}$) and independent of the other two parameters (n,a). The potential

function given by Eq. (374) satisfies always the requirement of Eq. (373) for any appropriate choice of the numerical values of the three parameters (n,ϵ,a). In particular, for the choice of $n = 10$, the lowest eigenvalue of Eq. (372) is given by $c = 0$ with the eigenfunction:

$$\langle \vec{r}|0\rangle = \frac{1}{r}\exp\left\{-\frac{3}{4}\left(\frac{a}{r}\right)^4\right\}, \quad (112,113)$$

so that we have exactly, for this eigenfunction,

$$\langle 0|\phi^{(L)}(|\vec{r}|)|0\rangle = -\frac{1}{m}\langle 0|\vec{p}^2|0\rangle. \quad (375)$$

It is, from the study of virial coefficient, concluded that we have most likely

$$9 \leqq n \leqq 12 \quad .^{(111,114)} \quad (376)$$

The numerical values of (ϵ,a) depend upon the choice of the parameter n.[111,113] There is a belief that the conventional choice of $n = 12$ is not quite as good to describe, at least, the thermodynamical properties of the noble (rare) elements, and also $n = 9$.[113] It seems that the choice of $n = 10$ is likely better than that of $n = 12$ from the conjecture obtained on the basis of Eq. (375).[113] Nevertheless, let us have the conventional choice of $n = 12$ in our further discussion as long as we have no lucid theoretical basis for the choice of the parameter n. Then, the potential of Eq. (374) takes the following more concrete form:

$$\phi^{(L)}(r) = 4\epsilon[(\frac{a}{r})^{12} - (\frac{a}{r})^6]. \quad (377)$$

We calculate the quasi-quantum effective potential $\phi_e^{(L)}(r)$ of this

Lennard-Jones 12-6 potential given in Eq. (300). The result is, after a simple calculation, obtained as follows:

$$\beta\phi_e^{(L)}(r) = \frac{4T_0}{T}\left[\left\{\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r}\right)^{6}\right\}\right.$$

$$+ \frac{T_1}{T}\left\{11\cdot 12\cdot\left(\frac{a}{r}\right)^{14} - 5\cdot 6\cdot\left(\frac{a}{r}\right)^{8}\right\}$$

$$\left. + \frac{9}{10}\left(\frac{T_1}{T}\right)^2\left\{11\cdot 12\cdot 13\cdot 14\cdot\left(\frac{a}{r}\right)^{16} - 5\cdot 6\cdot 7\cdot 8\cdot\left(\frac{a}{r}\right)^{10}\right\}\right], \qquad (378)$$

where the parameter a and the distance r are measured in the unit of $\mathring{A}$ and

$$T_0 \overset{\text{def.}}{=} \epsilon/k(^{\circ}K), T_1 \overset{\text{def.}}{=} 4{:}0113/(a^2 W)(^{\circ}K), \qquad (379)$$

and we have referred to the numerical values of the physical constants due to DuMond.[115] Several authors suggested the most probable numerical values of the two parameters (T_0, a). Among them, we choose the numerical values proposed recently by Rowlinson.[116] It is as follows:

$$T_0 = 35{\cdot}8(^{\circ}K),\ a = 2{\cdot}75(\mathring{A}). \qquad (380)$$

Another reliable intermolecular potential of the neon element is the Buckingham-Corner 6-exp. potential[117] modified recently by Rice and Hirschfelder on the basis of the extensive investigation of the second virial coefficient.[118] This modified Buckingham-Corner 6-exp. potential $\phi^{(B)}(r)$ is given by

$$\phi^{(B)}(r) = \begin{cases} \infty, & (r < r_{max.}) \\ \dfrac{\epsilon}{1-6/b}\left[\dfrac{6}{b}\, e^{b(1-r/a)} - \left(\dfrac{a}{r}\right)^6\right], & (r \geqq r_{max.}), \end{cases} \qquad (381)$$

where (ϵ,a,b) are the three parameters to be determined by the experimental data, and $r_{max.}$ is the value of the intermolecular distance r where the potential function $\phi^{(B)}(r)$ takes its maximum value.
The curve tracing of this potential function may be seen from the cited paper (118). The function given in the interval $[r_{max.},\infty)$ of this potential decreases infinitely with the decrease of the value of r in another interval $(0,r_{max.})$. Therefore, we need another conjunction curve $\phi^{(B)}(r) = \infty$ in the interval $(0,r_{max.})$ in order to match with the repulsive property of the realistic potential. The depth of this potential is given simply by the value of the parameter ϵ (at r = a), and it is independent of the other two parameters (a,b) just as that in the Lennard-Jones 12-6 potential. The value of $r_{max.}$ can be found from

$$r_{max.} = ax \tag{382}$$

substituted by the root $x(\neq 1)$ of the following transcendental equation:

$$xe^{-\lambda x} = e^{-\lambda}, \quad (\lambda \equiv b/7) \quad . \tag{383}$$

We calculate the quasi-quantum effective potential $\phi_e^{(B)}(r)$ of the modified Buckingham-Corner 6-exp. potential given by Eq. (381). The result is, after a simple calculation, given as follows:

$$\begin{aligned}\beta\phi_e^{(B)}(r) = {} & \frac{b}{b-6}\cdot\frac{T_0}{T}\left[\frac{6}{b}e^{b(1-r/a)} - \left(\frac{a}{r}\right)^6\right] \\ & + \frac{T_1}{T}\left\{6\left(b-\frac{2a}{r}\right)e^{b(1-r/a)} - 5\cdot 6\cdot\left(\frac{a}{r}\right)^8\right\} \\ & + \frac{9}{10}\left(\frac{T_1}{T}\right)^2\left\{6b^2\left(b-\frac{4a}{r}\right)e^{b(1-r/a)} - 5\cdot 6\cdot 7\cdot 8\cdot\left(\frac{a}{r}\right)^{10}\right\}\Big] \\ & r \geq r_{max.} \quad ,\end{aligned} \tag{384}$$

where the parameter a and the distance r are measured in the unit of $\overset{\circ}{A}$, and

$$T_o \overset{\text{def}}{=} \epsilon/k(^\circ K),\quad T_1 \overset{\text{def}}{=} 4.0113/(a^2 W)(^\circ K). \tag{385}$$

Several authors suggested the most probable values of the three parameters (T_o, a, b) on the basis of the extensive study of the virial coefficient, viscosity, and solid state of the neon element.[35] Among them, we choose the numerical values proposed recently by Mason and Rice.[119] It is as follows:

$$T_o = 38.0(^\circ K),\quad a = 3.147(\overset{\circ}{A}),\quad b = 14.5 \text{ (dimensionless)}. \tag{386}$$

On the basis of these numerical values, we find

$$r_{max.} \doteqdot 0.6(\overset{\circ}{A}) \tag{387}$$

by applying Newton's method for finding the root x of Eq. (383), and correspondingly, the maximum value of the potential $\phi^{(B)}(r)$ is given by

$$\phi^{(B)}(r_{max.})/\epsilon \approx 5.0\times 10^4\ , \tag{388}$$

i.e. about 0.5×10^5 times its depth .

Next, we will calculate the part of the exchange effective potential $\phi^{\pm}_{ex}(r)$ in Eq. (300) by using Eq. (296), which is universal for all kinds of the quantum fluids. Since the monoatomic molecule of the neon element has totally 10(even number) electrons, and its isotopes except the two isotopes with the even mass numbers 20 and 22 has totally a very faint abundance, the neon fluid may be regarded as being composed

of the molecules, each of which is composed again of the even number (30 or 32) of the elementary particles, i.e. ($10e^- + 10p + 10n$), or ($10e^- + 10p + 12n$). Therefore, the neon fluid is very likely a boson system, and its exchange effective potential $\phi^+_{ex}(r)$ is given by

$$\phi^+_{ex}(r) \doteq -\frac{1}{\beta}\,\ell n(1 + e^{-r^2/2\alpha\beta}). \tag{389}$$

The calculated result of the part of the exchange effective potential $\phi^+_{ex}(r)$ in Eq. (300) by using Eq. (389) is as follows:[43]

$$\begin{aligned}
\beta\phi_{ex}(r) &\overset{\text{def}}{\equiv} \cdot\beta[\phi^+_{ex}(r)+(\alpha\beta/6)\nabla^2\phi^+_{ex}(r)+(9/10)\cdot(\alpha\beta/6)^2\nabla^2\nabla^2\phi^+_{ex}(r)] \\
&= -\ell n[1 + \exp(-\frac{T}{12T_1}\cdot\frac{r^2}{a^2})] \\
&+ \frac{1}{4}\,[1 - \tanh(\frac{T}{24T_1}\cdot\frac{r^2}{a^2}) - \frac{T}{18T_1}\cdot\frac{r^2}{a^2}\,\operatorname{sech}^2(\frac{T}{24T_1}\cdot\frac{r^2}{a^2})] \\
&- \frac{21}{160}\operatorname{sech}^2(\frac{T}{24T_1}\cdot\frac{r^2}{a^2})\Big[1 - \frac{1}{378}\,(\frac{T}{T_1}\cdot\frac{r^2}{a^2})^2 - \frac{31T}{126T_1}\cdot\frac{r^2}{a^2} \\
&\times \tanh(\frac{T}{24T_1}\cdot\frac{r^2}{a^2}) + \frac{1}{126}\,(\frac{T}{T_1}\cdot\frac{r^2}{a^2})^2\tanh^2(\frac{T}{24T_1}\cdot\frac{r^2}{a^2})\Big],
\end{aligned} \tag{390}$$

where we have defined

$$T_1 \overset{\text{def}}{\equiv} \cdot 4\cdot 0113/(a^2 W)(^oK). \tag{391}$$

We note here that

$$|\tanh x| \leq 1,\quad 0 \leq \operatorname{sech} x \leq 1,\quad \lim_{x\to\infty}(\tanh x, \operatorname{sech} x) = (1, \lim_{x\to\infty} 2e^{-x})\ .$$

Thus, we have determined two kinds of the quantum effective potentials of the neon elements, i.e. the Lennard-Jones quantum-effective

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[43] The complication in this tedious calculation can be reduced very much by introducing the hyperbolic functions.

potential $\phi_e^{+(L)}(r)$ given by

$$\beta\phi_e^{+(L)}(r) = \beta\phi_e^{(L)}(r) + \beta\phi_{ex}(r) \tag{392}$$

with Eqs. (390) and (398), and the modified Buckingham-Corner quantum-effective potential $\phi_e^{+(B)}(r)$ given by

$$\beta\phi_e^{+(B)}(r) = \beta\phi_e^{(B)}(r) + \beta\phi_{ex}(r) \tag{393}$$

with Eqs. (390) and (384).

The quantum radial distribution function $g_\beta(r)$ of the neon fluid in our approximation theory can, then by referring to Eq. (300), be computed numerically by

$$g_\beta(r) = \tilde{g}_\beta(r) + \frac{4\cdot0113}{WT}\cdot\frac{1}{r}\frac{d^2}{dr^2}[r\tilde{g}_\beta(r)]$$

$$+ \frac{1}{2}\left(\frac{4\cdot0113}{WT}\right)^2\cdot\frac{1}{r}\frac{d^4}{dr^4}[r\tilde{g}_\beta(r)] + O(10^{-32}), \tag{394}$$

with the numerical computation of the classical radial distribution function $\tilde{g}_\beta(r)$ defined by

$$\tilde{g}_\beta(r) \overset{\text{def}}{=\!=} A^{(c)}\int_{r'} d\tau'\, e^{-\beta\Phi_e(\beta;\vec{r})}$$

$$\Phi_e(\beta;\vec{r}) \overset{\text{def}}{=\!=} \frac{1}{2}\sum_{\lambda,\mu=1}^{N}(1-\delta_{\lambda\mu})\phi_e^{+(L,\text{or}B)}(r) \tag{395}$$

by means of the Fortran program for the integral equation given by Eq. (329) and Eq. (330). The numerical values of the six parameters:

$$(T_o, a, b, W, T, n) \tag{396}$$

to be needed for the numerical computation have been known already by Eqs. (386), (380), and (370), except the last two parameters, i.e. the temperature and particle density (T,n) of the neon fluid with which we are concerned.

Our program for this task is as follows:

(1) We use the following approximate equation:

$$g_\beta(r) \doteq \tilde{g}_\beta(r) + \frac{4.0113}{WT} \frac{1}{r} \frac{d^2}{dr^2} [r\tilde{g}_\beta(r)]. \tag{397}$$

(2) We compute for the following four cases:

$T(^oK)$	44.2	39.4	33.1	24.7
$n(10^{-2}/\text{Å}^3)$	2.000	2.747	3.251	3.723

(398)

(3) We use the Fortran programs for the PY-, and CHNC-approximations.[120]

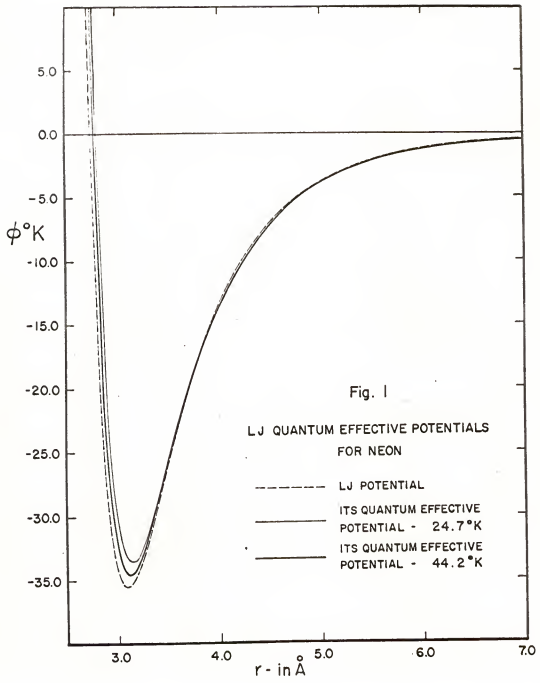
(4) We will compare our theoretical results of computations with the experimental result obtained from the measurement of the scattering intensity of x-rays by the neon liquid[121] by using Eq. (369).[122]

We will, in the next section, have our conclusion on the basis of the comparison of the theoretical result with the experimental result.

3.6. The Results of Computation and Comparison, and Conclusion

We start with explaining the figures obtained from the numerical calculation by IBM 709 computing machine. Fig. 1 shows the Lennard-Jones 6-12 pair potential and its quantum-effective pair potential for neon fluid given by Eq. (392) at two temperatures $44.2^{\circ}K$ and $24.7^{\circ}K$. The quantum-effective pair potentials at other two temperatures $39.4^{\circ}K$ and $33.1^{\circ}K$ are omitted in order to keep the clarity of the figure. However, their positions are between two curves of $44.2^{\circ}K$ and $24.7^{\circ}K$ with the curve of the higher temperature $39.4^{\circ}K$ closer to that of $44.2^{\circ}K$ than that of $24.7^{\circ}K$ does. The ordinate is measured by the unit of the Boltzman constant k (so it takes the unit of $^{\circ}K$), and the abscissa, by the unit of $\mathring{A}$. The curve of the original Lennard-Jones 6-12 pair potential can be regarded as the limiting position of its quantum-effective pair potential as the temperature $T \to \infty$. It is, from Fig. 1, observed easily that the bottom point of the quantum-effective potential runs along a path directed to the right-side and upward as T decreases.

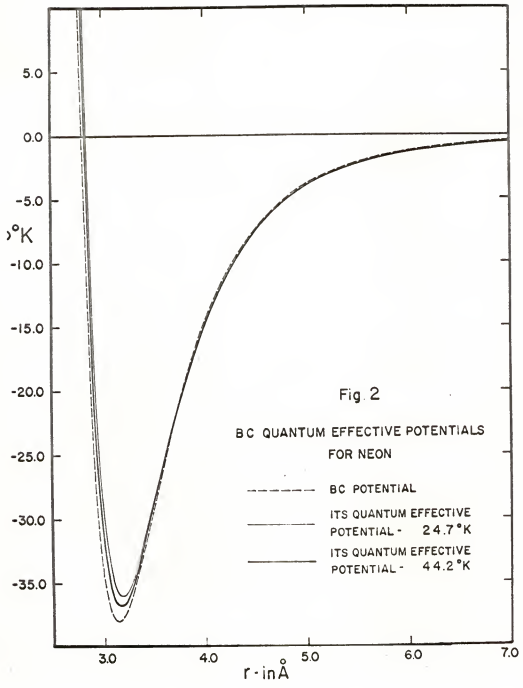
The lower the temperature, the shallower the depth of the quantum-effective potential and the narrower the width of it. Thus, the quantum effect on the original potential makes it shallower and narrower. The quantum-effective potentials at all temperatures are almost coincident with its original potential at a large distance r. This can be easily recognized also from the analytical form of the quantum-effective potential given by Eq. (392). Therefore, the contribution of the quantum-effective potential to the change of the radial

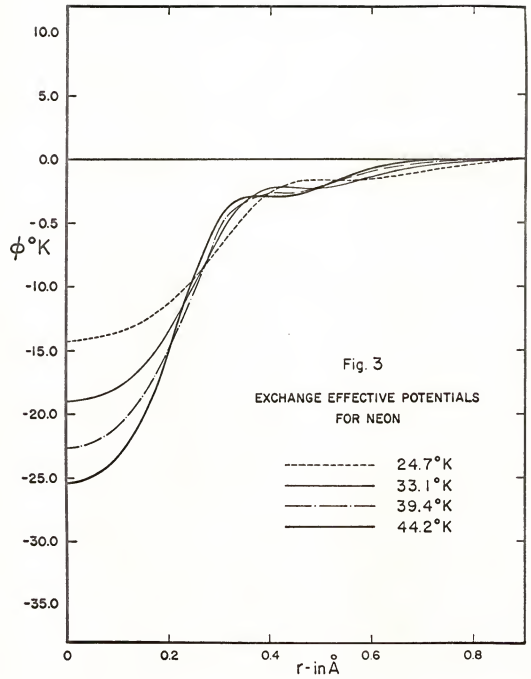

5.0
0.0
-5.0
-10.0
-15.0
-20.0
-25.0
-30.0
-35.0
φ°K
3.0
4.0
5.0
6.0
7.0
r - in Å
Fig. I
LJ QUANTUM EFFECTIVE POTENTIALS FOR NEON
LJ POTENTIAL
ITS QUANTUM EFFECTIVE POTENTIAL - 24.7°K
ITS QUANTUM EFFECTIVE POTENTIAL - 44.2°K

distribution function comes mainly from its parts within a short distance ($\approx 10\text{Å}$). The same feature appears also in the modified Buckingham-Corner 6-exp pair potential and its quantum-effective potential given by Eq. (393) as shown in Fig. 2. The quantum-effective potential of the modified Buckingham-Corner 6-exp pair potential has a depth deeper and width narrower than those of the quantum-effective potential of the Lennard-Jones 6-12 pair potential. The bottom points of the quantum-effective potentials of the Lennard-Jones 6-12 and modified Buckingham-Corner 6-exp pair potentials at $T=24.7^{\circ}K$ are located at the distances 3.15 Å and 3.19 Å, respectively, and the depth of the former is shallower than that of the latter. These values giving the mechanical equilibrium position of a neon monoatomic molecule relative to another molecule are comparable with the characteristic distance 3.196Å ($\equiv 4.52/\sqrt{2}$) between nearast neighbour ions of neon crystal with the face centered cubic of the lattice constant 4.52Å at $20.2^{\circ}K$.

This different feature of the two potentials suggested for the neon fluid make correspondingly a difference between their quantum radial distribution functions.

Figure 3 shows the exchange-effective potential of the neon fluid (likely a boson system) given by Eq. (390). The depth and width of it has the same feature as those of the quantum-effective potentials as the temperature changes. As shown in Fig. 3, the exchange-effective potential is effective in the region within a very short distance($\approx 1\text{Å}$) where the quantum-effective potential takes almost the value of infinity ∞. Therefore, it does not give any appreciable effect on the


5.0
0.0
-5.0
°K
-10.0
-15.0
-20.0
-25.0
-30.0
-35.0
3.0
4.0
5.0
6.0
7.0
r - in Å
Fig. 2
BC QUANTUM EFFECTIVE POTENTIALS FOR NEON
BC POTENTIAL
ITS QUANTUM EFFECTIVE POTENTIAL - 24.7 °K
ITS QUANTUM EFFECTIVE POTENTIAL - 44.2 °K


10.0
5.0
0.0
-0.5
-10.0
-15.0
-20.0
-25.0
-30.0
-35.0
φ°K
0
0.2
0.4
0.6
0.8
r-in Å
Fig. 3
EXCHANGE EFFECTIVE POTENTIALS
FOR NEON
24.7°K
33.1°K
39.4°K
44.2°K

quantum-radial distribution function of the neon fluid. Thus, the neon fluid can be regarded as a quasi-quantum fluid.

It is instructive to note again here that the functional form of the quantum-effective potential resulting from our theory is dependent on neither the particle density n nor the distance r between two molecules if the original pair potential of the fluid under consideration does. This property comes from the tacit assumption that the fluid under consideration is composed of identical, rigid and spherically symmetric molecules with a finite size and no internal structure. This is likely the case at the absolute zero temperature, or in the rarefied fluid, since every molecule is exactly at its ground state of a rigid structure at $0^{o}K$ and has no significant influence from any other molecule in a rarefied fluid. For example, the monoatomic molecule of neon element has the spherical electron-configuration $1s^{2}2s^{2}2p^{6}$ of a rigid structure at $0^{o}K$. In practice, the functional form of the original pair potential is likely to be dependent upon not only the particle density but also the temperature and the distance region between two molecules of the fluid under consideration, and therefore, so does its quantum-effective potential, since the internal structure of a molecule is dependent upon not only the distance from nearby molecules bringing their mutually induced moments, but also the temperature of the fluid giving rise to change of the internal molecular quantum-states of all molecules.[44] This realistic situation of the potential

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[44] The induced moment would be increased with the decrease of the distance and the symmetry of the geometrical configuration between molecules, and the statistical size of a molecule would be increased with an easier flexibility of its internal structure as the temperature increases.

between molecules would be a cause of discrepancy between the theoretical and experimental radial distribution functions of a fluid, even if we have known the method of determining the exact radial distribution function. However, we are, in this dissertation, dealing with the problem of low temperatures so that every individual molecule in the system is likely at its gound state and therefore the two potentials suggested above are well applicable in our problem. With this preparatory knowledge, we are going to look at 11 figures from Figs. 4 to 15.

Figure 4 shows the quantum radial distribution functions at $44.2^{o}K$ with the approximation of W.K.B. method and PY-integral equation. The bold curve is of the Lennard-Jones 6-12 pair potential and the dotted curve is of the modified Buckingham-Corner 6-exp pair potential. Of course, these two curves are the results obtained by our theory of W.K.B. approximation. It will be, hereafter in all graphs from Fig. 4 to Fig. 15, understood that the curves corresponding to the names of LJ andBC potentials represent those corresponding to the Lennard-Jones and Modified Buckingham-Corner pair potentials by our theory of W.K.B. approximation, and the corresponding classical curve is distinguished by writing the word "classical" right before the name of it in the corresponding graph. The convergency of R.M.S. in the course of the iterated computation is very rapid. The experimental radial distribution function (small circles) and the theoretical classical radial distribution function of the Lennard-Jones 6-12 pair potential computed by CHNC-integral equation are added for their comparisons with each other. The abscissa represents the relative distance

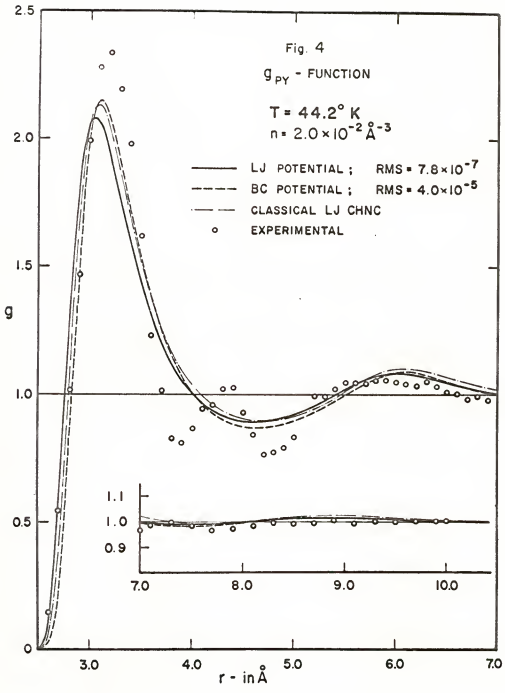
Fig. 4
g_{PY} - FUNCTION
T = 44.2° K
n = 2.0×10⁻² Å⁻³
LJ POTENTIAL ; RMS = 7.8×10⁻⁷
BC POTENTIAL ; RMS = 4.0×10⁻⁵
CLASSICAL LJ CHNC
EXPERIMENTAL
g
r - in Å
2.5
2.0
1.5
1.0
0.5
0
3.0
4.0
5.0
6.0
7.0
1.1
1.0
0.9
7.0
8.0
9.0
10.0

between two molecules and is measured in the unit of $\mathring{A}$. The ordinate represents the dimensionless values of the radial distribution function. The first maximum of the experimental curve appears at $r \doteqdot 3.2\mathring{A}$. (This is the position of a nearest neighbour of an ion in neon crystal) with $g_{max.} \doteqdot 2.33$. On the other hand, the maximum of the theoretical curve of the modified Buckingham-Corner 6-exp pair potential better than others appears at $r = 3.1\mathring{A}$ with $g_{max.} = 2.14$. The percentages of the errors of the theoretical r and $g_{max.}$ relative to their experimental values are within 3.2 per cent and 8.2 per cent, respectively. This little disagreement may be corrected by adjusting, a little more, the parameters contained in the used pair potential. Let us look at the features of both classical and quantum radial distribution curves for the Lennard-Jones 6-12 pair potential. The gap between them may be explained due to the quantum effect. To our surprise, it seems that the classical curve is in better agreement with the experimental curve than the quantum curve, giving a little suspect of the validity of the principles of quantum statistical mechanics for the realistic case. According to the view-point of the author of this dissertation, it seems that the worse agreement of the quantum curve does not originate essentially from the non-validity of quantum statistical mechanics, but presumably from the non-exact character of the Lennard-Jones 6-12 pair potential and the W.K.B. approximation of the quantum-theoretical radial distribution function in addition to the approximation of PY-, or CHNC-integral equation and also other erroneous origins. The worst discrepancy of all theoretical curves appears commonly in the region of the vicinity of the second minimum point, i.e. $r = 4.5\mathring{A}$. It is

worthwhile to note here that the region around r = $4.5\mathring{A}$ (= the lattice constant of neon crystal) is the area where the second nearest neighbours of an ion in neon crystal are found. Therefore, the theoretical curves must show its second maximum around this point of r $\doteqdot$ $4.5\mathring{A}$. In this sense, the experimental curve in this region is believed to be probably correct in agreement with the realistic property of the neon fluid that its monoatomic molecule is likely to move around in the region of the vicinity of the lattice point of its crystal at its liquid state. This theoretical discrepancy may be excluded much more by using the Monte Carlo method, or finding a more improved method than those of PY- and CHNC-integral equations and also our W.K.B. theory.

Figure 5 shows the case of the temperature T = $39.4^{\circ}K$, and it is seen that there is, as a whole, a fairly good agreement between the quantum-theoretical and experimental curves at this temperature. This indicates that the modified Buckingham-Corner 6-exp pair potential is likely to be more suitable at this temperature than the Lennard-Jones 6-12 pair potential. However, the disagreement between the theoretical and experimental curves appears also in the region of the lattice constant of neon crystal even in this case.

Since the last two cases of the temperatures $33.1^{\circ}K$ and $24.7^{\circ}K$ are those of fairly low temperatures close to the temperature $20.2^{\circ}K$ of the solid state of neon, a wider comparison has been made for all curves of the experimental and theoretical (both classical and quantum) radial distribution functions corresponding to both of the Lennard-Jones 6-12 and modified Buckingham-Corner 6-exp pair potentials as well as the approximations of PY- and CHNC-integral equations in each case of these two temperatures.

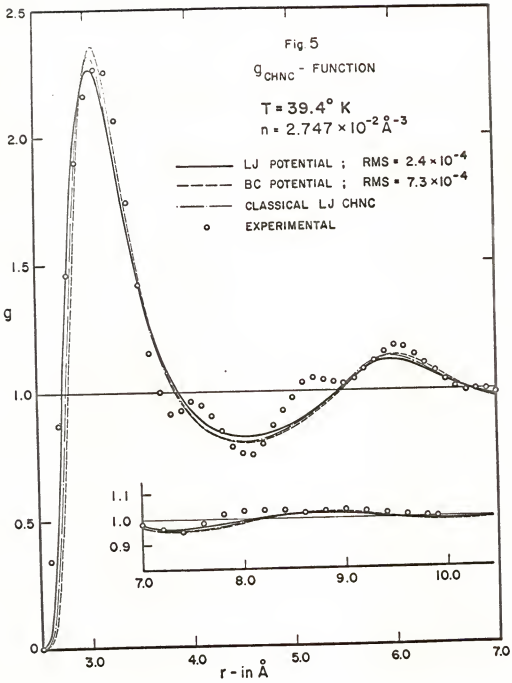
Fig. 5
g_{CHNC} - FUNCTION
T = 39.4° K
n = 2.747 × 10⁻² Å⁻³
LJ POTENTIAL ; RMS = 2.4 × 10⁻⁴
BC POTENTIAL ; RMS = 7.3 × 10⁻⁴
CLASSICAL LJ CHNC
EXPERIMENTAL
g
r - in Å
2.5
2.0
1.5
1.0
0.5
0
3.0
4.0
5.0
6.0
7.0
1.1
1.0
0.9
7.0
8.0
9.0
10.0

Figures 6 and 7 show those of the approximations of PY- and CHNC-integral equations at the temperature $33.1^{o}K$ respectively. The comparison of these figures shows us that the quantum curve computed from the approximation of the CHNC-integral equation by using the modified Buckingham-Corner 6-exp pair potential is much better than those of others with the possibility of the prediction of the almost correct value of the lattice constant of neon crystal according to the careful reading of the vlaue r where its first sharp maximum point appears. The common discrepancy in the region around the lattice point of the neon crystal grows up more again than the case of the temperature $39.4^{o}K$ in the order comparable with the case of the temperature $44.2^{o}K$.

Figures 8 and 9 show those of the approximations of PY- and CHNC-integral equations at the low temperature $24.7^{o}K$ very close to the temperature $20.2^{o}K$ of the solid state of neon element. The comparison shows us that the theoretical curves are not in so serious disagreement with the experimental curve. It seems that the theoretical curve computed from the approximation of the CHNC-integral equation by using the modified Buckingham-Corner 6-exp potential is, as a whole, in much better agreement with the experimental curve than the others, even though its maxima are higher, and its minima, lower than those of others relative to their experimental values.

Next, we will summarize the main common features obtained from our observation of the foregoing six figures as follows:

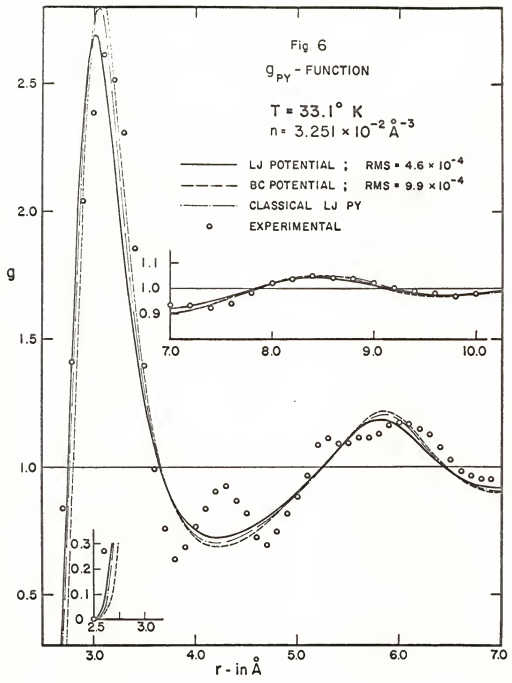
Fig 6
g_{PY} - FUNCTION
T = 33.1° K
n = 3.251 × 10⁻² Å⁻³
LJ POTENTIAL ; RMS = 4.6 × 10⁻⁴
BC POTENTIAL ; RMS = 9.9 × 10⁻⁴
CLASSICAL LJ PY
EXPERIMENTAL
g
r - in Å

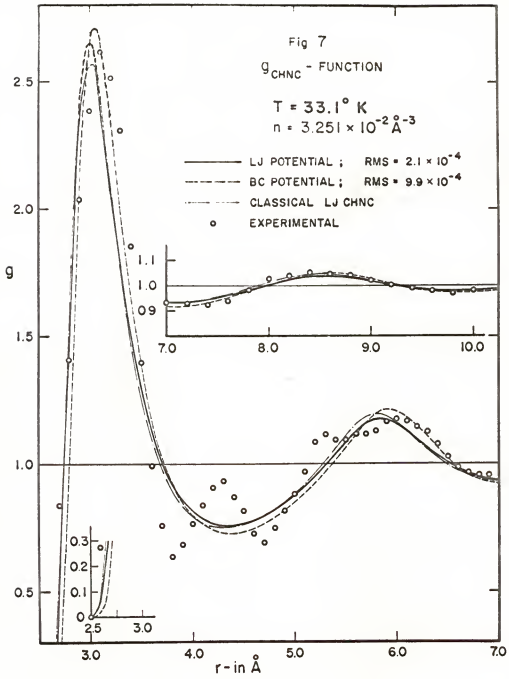
Fig 7
g_{CHNC} - FUNCTION
T = 33.1° K
n = 3.251 × 10⁻² Å⁻³
LJ POTENTIAL ; RMS = 2.1 × 10⁻⁴
BC POTENTIAL ; RMS = 9.9 × 10⁻⁴
CLASSICAL LJ CHNC
EXPERIMENTAL
g
r - in Å
2.5
2.0
1.5
1.0
0.5
3.0
4.0
5.0
6.0
7.0
1.1
1.0
0.9
7.0
8.0
9.0
10.0
0.3
0.2
0.1
0
2.5
3.0

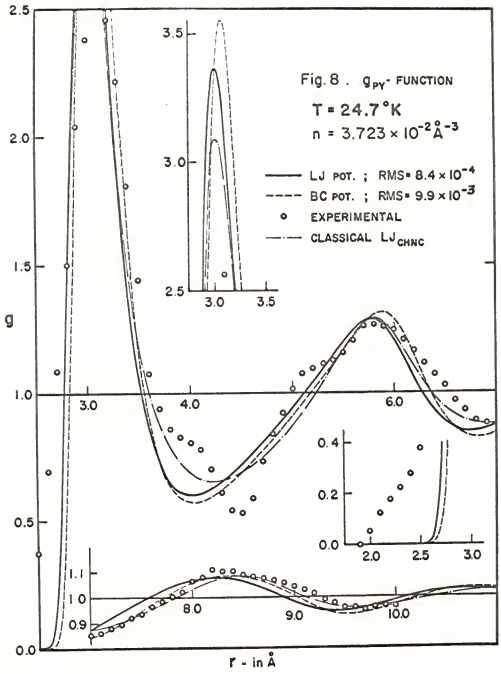
Fig. 8 . g_{PY}- FUNCTION
T = 24.7°K
n = 3.723 × 10^{-2} Å^{-3}
LJ POT. ; RMS= 8.4 × 10^{-4}
BC POT. ; RMS= 9.9 × 10^{-3}
EXPERIMENTAL
CLASSICAL LJ$_{CHNC}$
g
r - in Å

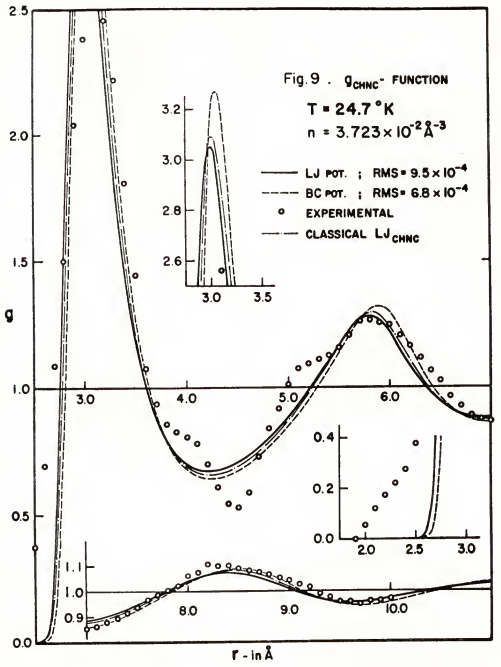
Fig.9 . g_{CHNC}- FUNCTION
T = 24.7 °K
n = 3.723 × 10^{-2} Å^{-3}
LJ POT. ; RMS = 9.5 × 10^{-4}
BC POT. ; RMS = 6.8 × 10^{-4}
EXPERIMENTAL
CLASSICAL LJ_{CHNC}
g
r - in Å

(1) The values of r at which the theoretical curve takes its extrema are, as a whole, much closer to its experimental values in the case of the modified Buckingham-Corner 6-exp pair potential than the Lennard-Jones 6-12 pair potential.

(2) The maximum and minimum of the theoretical curve for the modified Buckingham-Corner 6-exp pair potential are always higher and lower than those of the Lennard-Jones 6-12 pair potential.

(3) The extrema of the function $|g_\beta(r)-1|$ in both potentials are lower at higher temperature, and higher at lower temperature than experimental values.

(4) The approximation of the CHNC-integral equation gives a better answer than that of PY-integral equation at lower temperature, and vice versa.

(5) The width of the first peak of the theoretical curve is broader at higher temperature and narrower at lower temperature than its experimental width in both potentials and the approximations of PY- and CHNC-integral equations.

(6) The feature of the discrepancy of the theoretical curve around the lattice point $r = 4.52\text{Å}$ of the face centered cubic characteristic to the neon crystal is almost the same, at least, at four temperatures tried.

(7) The gap between the theoretical and experimental curves becomes smaller and smaller with the increase of the distance r, while greater and greater with approaching to the diameter

$r \doteqdot 1.9\mathring{A}$ of the hard core of the intermolecular pair potential of the neon monoatomic molecules and lower temperature (look at Figs. 8 and 9).

It seems that the main origins causing the disagreement between the theoretical and experimental curves at the given four temperatures and particle densities come from the following several defects, if the Neumann's statistical density operator $\exp(-\beta H)/Q_\beta$ based on Schrödinger-Heisenberg quantum mechanics is absolutely correct for describing the statistical property of the natural world: Theoretically,

(a) The gap between the realistic potential and the idealized pair potential (Lennard-Jones 6-12, or modified Buckingham-Corner 6-exp pair potential) throughout all regions of r, temperature and particle density,

(b) The W.K.B. approximation of neglecting the part of the second order of α^2,

(c) The approximation of PY-, or CHNC-integral equation,

(d) The numerical method of the solution to the approximated PY-, or CHNC-integral equation by using the finite limit of integration (We have taken $20\mathring{A}$ for it.) and the finite increment Δr of the integration variable r (We have taken $0.05\mathring{A}$ for it.).

(e) The determination of the experimental radial distribution function from the experimental intensity curve of scattering x-rays by the numerical method according to Eq. (3?9) with a theoretical estimation of the scattering intensity of small angle, and experimentally,

(f) The possibility of various origins of unavoidable, inconceivable errors coming in the experimental measurement of the scattering intensity of x-rays,

(g) The experimental difficulty of determining exactly the scattering intensity of x-rays at the region of small scattering angle as stated by the experimentalist in their published paper.[121]

It is likely that the common features (1) and (2) stated previously tell us that the modified Buckingham-Corner 6-exp pair potential is superior to the Lennard-Jones 6-12 pair potential in describing the realistic statistical property of neon fluid up to a fairly low temperature. However, this is not uniquely the case. We will show below the correctness of this criteria. Let us look at Figs. 1 and 2 again. Certainly, the modified Buckingham-Corner 6-exp pair potential has a deeper depth at a larger distance r and wider width than those of the Lennard-Jones 6-12 pair potential. This difference has caused the different features of (1) and (2) in both potentials. Now, let us remember that, in the modified Buckingham-Corner 6-exp pair potential the depth, the value r minimizing the potential value and the width are determined by the numerical values of the three parameters (ϵ,a,b) of Eq. (381) respectively, while in the Lennard-Jones 6-12 pair potential, by the numerical values of the three parameters (ϵ,a,n) of Eq. (374), respectively. Therefore, we can make a better match of the theoretical radial distribution curve with its experimental curve equivalently in both potentials by adjusting suitably the numerical values of their three parameters, as long as we are concerned with the

radial distribution function in some regions of the distance r and temperature T.

Next, it is supposed that the discrepancy of the features (3), (4), (5), and (7) comes likely mainly from the combination of the error origins (a), (b), (e), and (g) with the most dominance of (e), since the origins (c), (d), and (f) are believed to cause a small error together with each other. The reasonableness of this criteria can be seen from the fact of the excellent agreement between the theoretical and experimental curves of the relative intensity of the scattering x-rays by the neon fluid as we will show in the next six figures, i.e. from Fig. 10 to Fig. 15. However, it is likely that the dominant disagreement of the sharp peak of the theoretical curve with the corresponding experimental curve at the temperature $24.7^{o}K$ (Figs. 8 and 9) is realistic and reveals us the limitation of the validity of the W.K.B. approximation according to the numerical discussion done already in p 95.[45]

The remaining six figures, i.e. from Fig. 10 to Fig. 15 show the comparison of the experimental curves of the relative intensity $J_{\beta}(n,K)$ of the scattering x-rays by the neon fluid with their theoretical curves calculated from Eq. (396), i.e.

$$J_{\beta}(n,K) = f(K)^2[1+\frac{n}{K}\int_0^{\infty} dr\{g_{\beta}(r)-1\}r \sin(4\pi Kr)], \qquad (399)$$

---

[45] The fact of the very slow convergency of R.M.S. in the course of computing this case by the IBM 709 Computer reveals also to us this limitation, and we remember that this temperature $24.7^{o}K$ is very close to the temperature $20.2^{o}K$ of the solid state of neon.

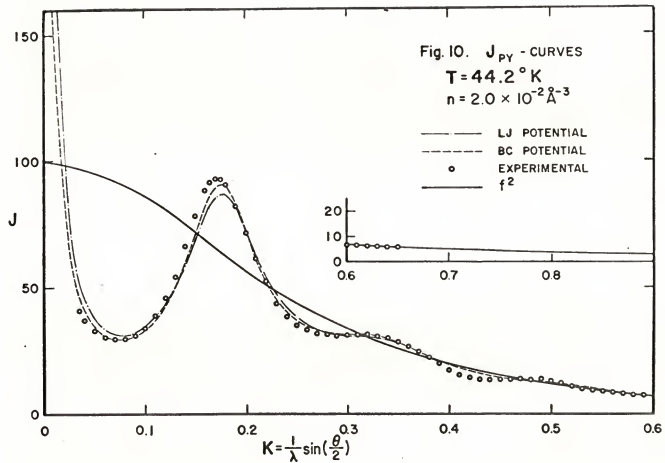
Fig. 10. J_{PY} - CURVES
T = 44.2 °K
n = 2.0 × 10^{-2} Å^{-3}
LJ POTENTIAL
BC POTENTIAL
EXPERIMENTAL
f^2
J
K = $\frac{1}{\lambda}\sin(\frac{\theta}{2})$
150
100
50
0
0
0.1
0.2
0.3
0.4
0.5
0.6
20
10
0
0.6
0.7
0.8

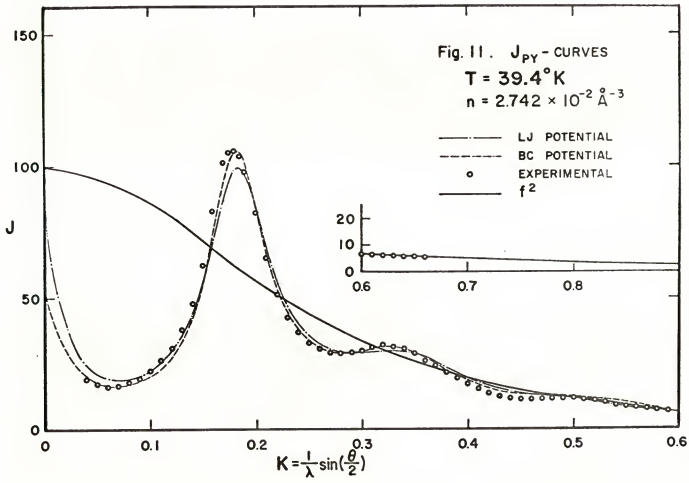
Fig. 11. J_{PY} - CURVES
T = 39.4°K
n = 2.742 × 10^{-2} Å^{-3}
LJ POTENTIAL
BC POTENTIAL
EXPERIMENTAL
f^2
J
K = $\frac{1}{\lambda}\sin(\frac{\theta}{2})$
150
100
50
0
0
0.1
0.2
0.3
0.4
0.5
0.6
20
10
0
0.6
0.7
0.8

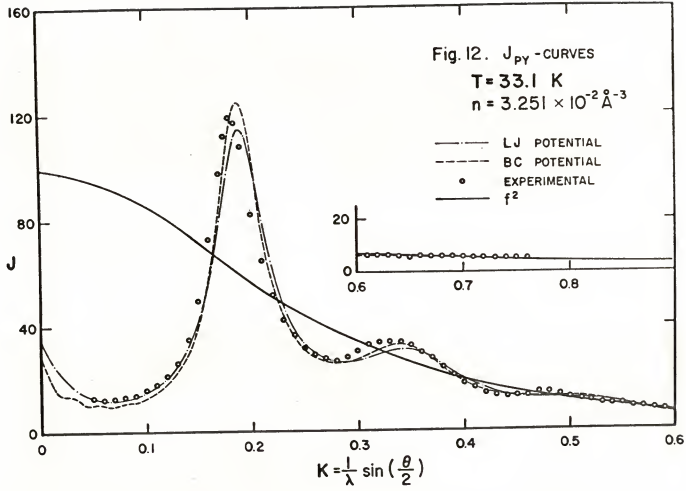
Fig. 12. J_{PY} - CURVES
T = 33.1 K
n = 3.251 × 10^{-2} Å^{-3}
LJ POTENTIAL
BC POTENTIAL
EXPERIMENTAL
f^2
J
K = $\frac{1}{\lambda}$ sin ($\frac{\theta}{2}$)
0
40
80
120
160
0.1
0.2
0.3
0.4
0.5
0.6
20
0.6
0.7
0.8

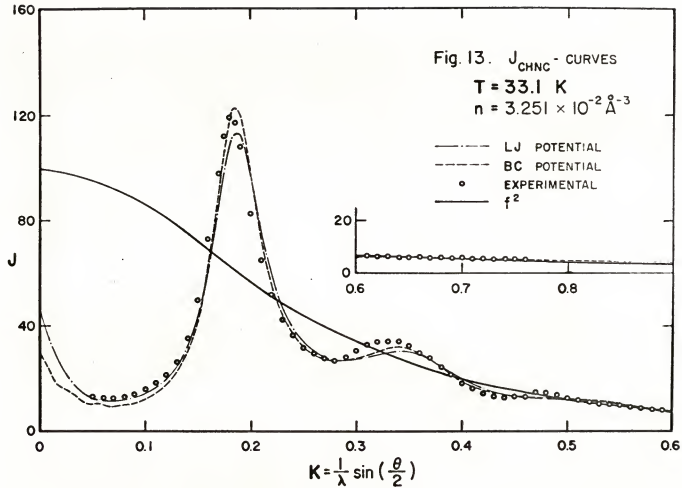
Fig. 13. J_{CHNC} - CURVES
T = 33.1 K
n = 3.251 × 10^{-2} Å^{-3}
LJ POTENTIAL
BC POTENTIAL
EXPERIMENTAL
f^2
J
$K = \frac{1}{\lambda} \sin\left(\frac{\theta}{2}\right)$
0
40
80
120
160
0.1
0.2
0.3
0.4
0.5
0.6
20
0.6
0.7
0.8

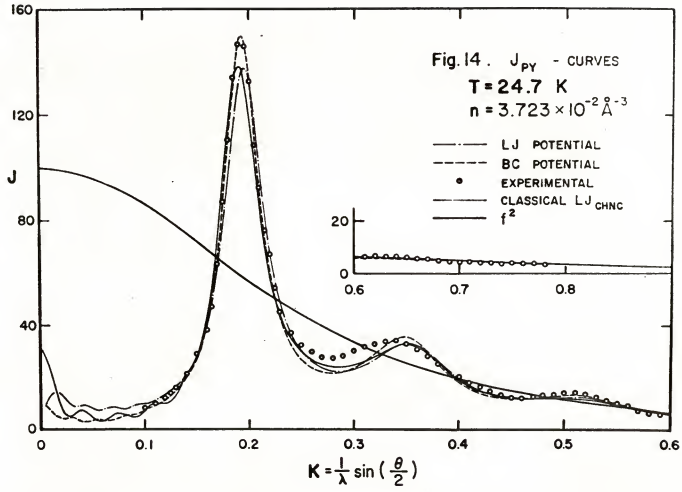
Fig. 14 . J_{PY} - CURVES
T = 24.7 K
n = 3.723 × 10⁻² Å⁻³
LJ POTENTIAL
BC POTENTIAL
EXPERIMENTAL
CLASSICAL LJ CHNC
f²
J
K = 1/λ sin (θ/2)
160
120
80
40
0
0.1
0.2
0.3
0.4
0.5
0.6
20
0.6
0.7
0.8

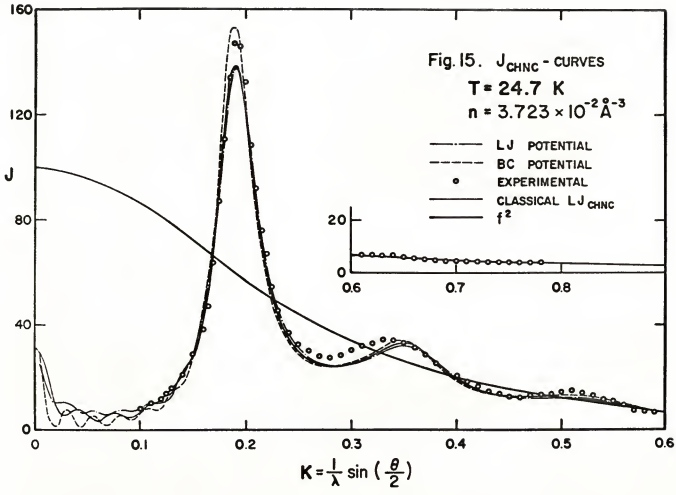
Fig. 15. J_{CHNC} - CURVES
T = 24.7 K
n = 3.723 × 10^{-2} Å^{-3}
LJ POTENTIAL
BC POTENTIAL
EXPERIMENTAL
CLASSICAL LJ CHNC
f^2
J
K = $\frac{1}{\lambda}$ sin ($\frac{\theta}{2}$)
0
40
80
120
160
0.1
0.2
0.3
0.4
0.5
0.6
20
0.6
0.7
0.8

where we have put

$$K \overset{\text{def}}{=\!=} \cdot \lambda^{-1} \sin(\theta/2), \quad \lambda = (\text{the wave length of scatering x-rays}),$$

$$J_\beta(n,K)/f(K)^2 \overset{\text{def}}{=\!=} \cdot I_\beta(n,K)/I(n,K). \tag{400}$$

We have, in the numerical calculation of Eq. (399), used the experimental curve of the atomic structure factor $f(K)^2$ obtained by the experimentalists of the quoted paper 121, and $r = 20\text{Å}$ as the upper limit of the integration of Eq. (399) instead of taking $r = \infty$ as we have discussed already in p 163 and p 164. Since we have, in the graphs of those from Fig. 4 to Fig. 7, not found clearly the difference between the quantum-theoretical and classical-theoretical curves at the higher temperatures $44.2^\circ K$, $39.4^\circ K$, and $33.1^\circ K$ than the temperature $24.7^\circ K$, we have drawn the classical-theoretical curve only in Figs. 14 and 15 corresponding to the lower temperature $24.7^\circ K$ in order to show clearly the validity of the quantum effect in the neon fluid. The first six figures, i.e., from Fig. 4 to Fig. 9 are nothing but the replica of these last six figures with the theoretical estimation of the scattering intensity of small angle region which was presumably the main origin causing various errors between the theoretical and experimental curves in them. As shown in the figures from Fig. 10 to Fig. 15, the agreement between our theory and the experiment is excellent, especially for the modified Buckingham-6orner 6-exp pair potential.[46] Let us look again at Fig. 14 and 15 corresponding to the

[46] A more excellent agreement is expected by adjusting suitably the atomic structure factor $f(K)^2$.

lowest temperature $24.7^{o}K$ in our four cases of temperature. The first peak of the quantum-theoretical intensity curve is almost completely in excellent agreement with the experimental intensity curve, while the classical-theoretical intensity curve shows clearly a considerable discrepancy. This fact implies that the neon fluid must be considered as a quantum fluid in the temperature region, at least, below the temperature $24.7^{o}K$, and the Buckingham-Corner 6-exp pair potential modified by Rice and Hirschfelder is more suitable than the Lennard-Jones 6-12 pair potential in describing the statistical property of neon. At this point, it is clear from the fact of the excellent agreement between our theoretical intensity curve and the experimental intensity curve to be pointed out that the theoretical estimation of the scattering intensity of small angle region done by the author of the quoted paper 122 must be studied thorougly again on the basis of our theory presented in this dissertation to exclude the main origin (e) of the various discrepancies stated previously.

Finally, we may conclude on the basis of the discussion done so far as follows: our theory of the quantum radial distribution function by the W.K.B. approximation is believed to give a good answer in agreement with experiment in the temperature region up to a fairly low temperature, and this assertion may be put on a stronger basis if the numerical computation will be done by using a more powerful method than those of the PY- and CHNC-integral equation and also a more improved potential than the Lennard-Jones 6-12 and modified Buckingham-Corner 6-exp pair potentials.

APPENDIX I

The reasonableness of this definition can be quaranteed also by the following discussions: Let us consider the expectation value $\langle Q \rangle$ of an observable (time-independent) Q. This is given by Eq. (13). We have, therefore,

$$\langle Q \rangle = \mathrm{Tr}(WQ) = \sum_{\vec{n}} \langle \vec{n} | \beta; t \rangle \langle \beta; t | Q | \vec{n} \rangle$$

$$= \sum_{\vec{n}} \langle \vec{n} | e^{-iHt/\hbar} | \beta \rangle \langle \beta | e^{iHt/\hbar} Q | \vec{n} \rangle$$

$$= \sum_{\vec{n}} e^{-i\omega_{\vec{n}} t} \langle \vec{n} | \beta \rangle \langle \beta | \left[\sum_{\vec{n}'} | \vec{n}' \rangle \langle \vec{n}' | \right] e^{iHt/\hbar} Q | \vec{n} \rangle$$

$$= \sum_{\vec{n}, \vec{n}'} e^{-i(\omega_{\vec{n}} - \omega_{\vec{n}'})t} \langle \vec{n} | \beta \rangle \langle \beta | \vec{n}' \rangle \langle \vec{n}' | Q | \vec{n} \rangle \ ,$$

which has the time-fluctuation. Let us, next, take the time-average of $\langle Q \rangle$ over whole time interval $(-\infty, \infty)$ by using the validity of the postulate of a priori probability. It gives us

$$\overline{\langle Q \rangle} = \sum_{\vec{n}, \vec{n}'} \langle \vec{n} | \vec{n}' \rangle \langle \vec{n} | \beta \rangle \langle \beta | \vec{n}' \rangle \langle \vec{n}' | Q | \vec{n} \rangle$$

$$= \sum_{\vec{n}'} \langle \vec{n}' | Q \Big(\sum_{\vec{n}} | \vec{n} \rangle | \langle \vec{n} | \beta \rangle |^2 \langle \vec{n} | \Big) | \vec{n}' \rangle$$

$$= \sum_{\vec{n}'} \langle \vec{n}' | QD_\beta | \vec{n}' \rangle$$

$$= \mathrm{Tr}(QD_\beta) = \mathrm{Tr}(D_\beta Q),$$

by using Eq. (40)'. We see, therefore, that

$$\overline{\mathrm{Tr}(QW)} = \mathrm{Tr}(QD_\beta) = \mathrm{Tr}(Q\overline{W}).$$

This fact gives us a statistical basis of reasonableness of Neumann's density operator D_β defined by Eq. (40).

APPENDIX II

Let us, at first, suppose a simple case that we have a system of three identical, indistinguishable particles, and consider the number of ways of distributing three particles in a generic distribution specified by three position-vectors $\vec{r}_1$, $\vec{r}_2$, $\vec{r}_3$ as shown in Fig. 1. Of course, there are $3!$, i.e six ways of distributing three particles in this specific generic distribution as shown in Fig. 2 below.

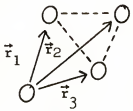

Fig. 1.

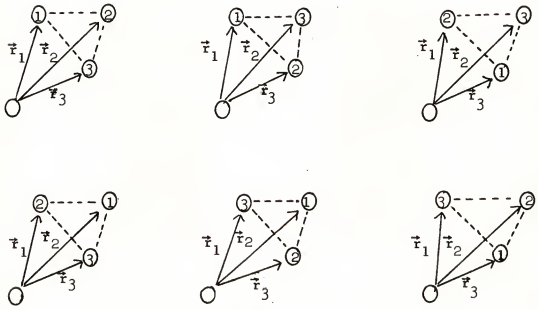

Fig. 2.

We note here that these six different kinds of distribution belong to a same generic distribution shown in Fig. 1. We may consider an operator $\vec{R}$ corresponding to the generic distribution of the system. This generic distribution may be symbolized formally by $(\vec{r}_1\vec{r}_2\vec{r}_3)$ with the associate law given by

$$(\vec{r}_1\vec{r}_2\vec{r}_3) = (\vec{r}_2\vec{r}_3\vec{r}_1) = (\vec{r}_3\vec{r}_1\vec{r}_2) = (\vec{r}_1\vec{r}_3\vec{r}_2) = (\vec{r}_3\vec{r}_2\vec{r}_1) = (\vec{r}_2\vec{r}_1\vec{r}_3),$$

since three points correspond to the positions of trio $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_3$ no matter how they are ordered. The symbols $(\vec{r}_1,\vec{r}_2,\vec{r}_3)$, $(\vec{r}_2,\vec{r}_1,\vec{r}_3)$, etc. are, therefore, not appropriate for the specification of generic distribution since this symbol involves, in it, not only the positions of trio but also their order. These latter symbols are fitted actually to represent the distributions of particles in such a way that, for example,

$$(\vec{r}_{\overset{1}{2}}\vec{r}_{\overset{2}{3}}\vec{r}_{\overset{3}{1}}), \text{ or briefly } (\vec{r}_2,\vec{r}_3,\vec{r}_1)$$

represents the distribution in which the particle 1 is at position $\vec{r}_2$, the particle 2 at position $\vec{r}_3$, and the particle 3 at position $\vec{r}_1$. We may represent the eigenket of the generic position-operator $\vec{R}$ corresponding to this distribution $(\vec{r}_2,\vec{r}_3,\vec{r}_1)$ by the symbol:

$$|_{\vec{r}_2,\vec{r}_3,\vec{r}_1}^{1\ 2\ 3}\rangle, \text{ or briefly } |\vec{r}_2,\vec{r}_3,\vec{r}_1\rangle \quad .$$

Hence the eigenvalue equations corresponding to the distribution shown in Fig. 2 may be represented by

$$\vec{R}|\vec{r}_1,\vec{r}_2,\vec{r}_3\rangle = (\vec{r}_1,\vec{r}_2,\vec{r}_3)|\vec{r}_1,\vec{r}_2,\vec{r}_3\rangle;\ \vec{R}|\vec{r}_1,\vec{r}_3,\vec{r}_2\rangle = (\vec{r}_1,\vec{r}_3,\vec{r}_2)|\vec{r}_1,\vec{r}_3,\vec{r}_2\rangle,$$

$$\vec{R}|\vec{r}_2,\vec{r}_3,\vec{r}_1\rangle = (\vec{r}_2,\vec{r}_3,\vec{r}_1)|\vec{r}_2,\vec{r}_3,\vec{r}_1\rangle;\ \vec{R}|\vec{r}_2,\vec{r}_1,\vec{r}_3\rangle = (\vec{r}_2,\vec{r}_1,\vec{r}_3)|\vec{r}_2,\vec{r}_1,\vec{r}_3\rangle,$$

$$\vec{R}|\vec{r}_3,\vec{r}_1,\vec{r}_2\rangle = (\vec{r}_3,\vec{r}_1,\vec{r}_2)|\vec{r}_3,\vec{r}_1,\vec{r}_2\rangle;\ \vec{R}|\vec{r}_3,\vec{r}_2,\vec{r}_1\rangle = (\vec{r}_3,\vec{r}_2,\vec{r}_1)|\vec{r}_3,\vec{r}_2,\vec{r}_1\rangle.$$

If the system under consideration is composed of three identical, distinguishable particles, these six distributions symbolized by $(\vec{r}_1,\vec{r}_2,\vec{r}_3)$, $(\vec{r}_1,\vec{r}_3,\vec{r}_2)$, $(\vec{r}_2,\vec{r}_3,\vec{r}_1)$, $(\vec{r}_2,\vec{r}_1,\vec{r}_3)$, $(\vec{r}_3,\vec{r}_1,\vec{r}_2)$, and $(\vec{r}_3,\vec{r}_2,\vec{r}_1)$ are all physically different, but if the system is composed of identical indistinguishable particles, then these six distributions are all physically the same, and may be represented by the symbol $(\vec{r}_1\vec{r}_2\vec{r}_3)$ or briefly $\vec{r}$ stated above. Then, the above six eigenvalue equations are written as

$$\vec{R}|\vec{r}_1,\vec{r}_2,\vec{r}_3\rangle = \vec{r}|\vec{r}_1,\vec{r}_2,\vec{r}_3\rangle,\quad \vec{R}|\vec{r}_1,\vec{r}_3,\vec{r}_2\rangle = \vec{r}|\vec{r}_1,\vec{r}_3,\vec{r}_2\rangle,$$

$$\vec{R}|\vec{r}_2,\vec{r}_3,\vec{r}_1\rangle = \vec{r}|\vec{r}_2,\vec{r}_3,\vec{r}_1\rangle,\quad \vec{R}|\vec{r}_2,\vec{r}_1,\vec{r}_3\rangle = \vec{r}|\vec{r}_2,\vec{r}_1,\vec{r}_3\rangle,$$

$$\vec{R}|\vec{r}_3,\vec{r}_1,\vec{r}_2\rangle = \vec{r}|\vec{r}_3,\vec{r}_1,\vec{r}_2\rangle,\quad \vec{R}|\vec{r}_3,\vec{r}_2,\vec{r}_1\rangle = \vec{r}|\vec{r}_3,\vec{r}_2,\vec{r}_1\rangle.$$

This fact implies that the generic distribution of particles is $3!$ fold-degenerate in the system of three identical, indistinguishable particles. Now, let Π_{12} be the permutation operator (exchange operator) permuting #1 and #2 particles. It is, then, by noting no dependence of $\vec{r}$ on Π_{12} in the system of identical indistinguishable particles, that we can have

$$\Pi_{12}\vec{R}|\vec{r}_1,\vec{r}_2,\vec{r}_3\rangle = \Pi_{12}\vec{r}|\vec{r}_1,\vec{r}_2,\vec{r}_3\rangle = \vec{r}\Pi_{12}|\vec{r}_1,\vec{r}_2,\vec{r}_3\rangle$$

$$= \vec{r}|\vec{r}_2,\vec{r}_1,\vec{r}_3\rangle = \vec{R}|\vec{r}_2,\vec{r}_1,\vec{r}_3\rangle = \vec{R}\Pi_{12}|\vec{r}_1,\vec{r}_2,\vec{r}_3\rangle\ ,$$

$$\therefore\ \Pi_{12}\vec{R} = \vec{R}\Pi_{12},\quad \text{or}\quad [\vec{R},\Pi_{12}] = 0.$$

This can be extended to the system of N identical, indistinguishable particles. We have, thus for an arbitrary permutation operator Π,

$$[\vec{R},\Pi] = 0,$$

where $\vec{R}$ is the generic position-operator of the system corresponding to its generic distribution, and the eigenvalue $\vec{r}$ of $\vec{R}$ represents the physical distribution of N particles in the realistic space. This point of view may be extended also to the generic momentum-and spin-operators $(\vec{P},\vec{\Sigma})$ of the system.

APPENDIX III

The proof of the Laplace integral given by

$$J = \int_{\infty} d^{3N}\vec{k}\, e^{-a\vec{k}^2+i\vec{c}\cdot\vec{k}} = (\frac{\pi}{a})^{3N/2} e^{-\vec{c}^2/4a}$$

is as follows: Since we have

$$\exp(-a\vec{k}^2+i\vec{c}\cdot\vec{k}) = \prod_{\lambda=1}^{N} \exp(-a\vec{k}_\lambda^2+i\vec{c}_\lambda\cdot\vec{k}_\lambda),$$

$$d^{3N}\vec{k} = \prod_{\lambda=1}^{N} d^3\vec{k}_\lambda,$$

the integral J can be split into the product of N equivalent 3-dimensional integrals. This 3-dimensional integral can be split also into the product of three equivalent one-dimensionl integrals. We have thus

$$J = \prod_{\lambda=1}^{N} \left[\prod_{j=1}^{3} \int_{-\infty}^{\infty} dx\, e^{-ax^2+ic_\lambda^{(j)}x} \right] . \qquad (1)$$

Now, let us consider the Laplace's integral $J_\lambda^{(j)}$ defined by

$$J_\lambda^{(j)} = \int_{-\infty}^{\infty} dx\, e^{-ax^2+ic_\lambda^{(j)}x} . \qquad (2)$$

The use of the Euler's theorem give us

$$J_\lambda^{(j)} = \int_{-\infty}^{\infty} dx\ e^{-ax^2} \cos(c_\lambda^{(j)} x) + i \int_{-\infty}^{\infty} dx\ e^{-ax^2} \sin(c_\lambda^{(j)} x),$$

or

$$J_\lambda^{(j)} = \int_{-\infty}^{\infty} dx\ e^{-ax^2} \cos(c_\lambda^{(j)} x) \tag{3}$$

by noting that $\exp(-ax^2)$ = (even function), $\sin(c_\lambda^{(j)} x)$ = (odd function) which makes the second integral be zero. Now, we differentiate Eq. (3) with respect to the parameter $c_\lambda^{(j)}$, and then integrate by parts, to have

$$J_\lambda^{(j)\prime} = [e^{-ax^2} \cdot (2a)^{-1} \cdot \sin(c_\lambda^{(j)} x)]_{-\infty}^{\infty} - (c_\lambda^{(j)} J_\lambda^{(j)}/2a),$$

or

$$dJ_\lambda^{(j)}/J_\lambda^{(j)} = - c_\lambda^{(j)} dc_\lambda^{(j)}/2a.$$

This gives, on integrating it, us the result given by

$$J_\lambda^{(j)} = A \exp(-c_\lambda^{(j)2}/4a), \tag{4}$$

and the constant A of integration can be determined by combining Eqs. (4) and (3), and then putting $c_\lambda^{(j)} = 0$ on both-hand sides. It is as follows:

$$A = \int_{-\infty}^{\infty} dx\ e^{-ax^2} = \text{(the probability integral)} = \sqrt{\pi/a}. \tag{5}$$

We have, from Eqs. (5), (4), (2), and (1), finally

$$J = \prod_{\lambda=1}^{N}\left[\prod_{j=1}^{3}(\pi/a)^{\frac{1}{2}}\exp(-c_\lambda^{(j)2}/4a)\right]$$

$$= (\pi/a)^{3N/2}\exp(-\sum_{\lambda=1}^{N}\sum_{j=1}^{3} c_\lambda^{(j)2}/4a) = (\pi/a)^{3N/2}\exp(-\vec{c}^{\,2}/4a).$$

It is noticeable that the integral given by Eq. (2) can be obtained formally from the probability integral by the following procedure:

$$\int_{-\infty}^{\infty} dx\ e^{-ax^2+icx} = \int_{-\infty}^{\infty} dx\ e^{-c^2/4a}\cdot e^{-a(x-ic/2a)^2}$$

$$= \exp(-c^2/4a)\cdot a^{-\frac{1}{2}}\int_{-\infty}^{\infty} dy\ \exp(-y^2)$$

$$= (\pi/a)^{\frac{1}{2}}\exp(-c^2/4a).$$

The same formal procedure is applicable for the following Fresnel's integral appearing in the physical optics:

$$\int_{-\infty}^{\infty} dx\ \exp(ix^2) = \sqrt{i}\int_{-\infty}^{\infty} dx\ \exp(-[\sqrt{-i}x]^2)d(\sqrt{-i}x)$$

$$= \sqrt{i}\int_{-\infty}^{\infty} dy\ \exp(-y^2) = \frac{1+i}{\sqrt{2}}\cdot\sqrt{\pi}\ ,$$

$$\int_{-\infty}^{\infty} dx\ \sin x^2 = \int_{-\infty}^{\infty} dx\ \cos x^2 = \sqrt{\pi/2}\ ,$$

by noting that $\exp(ix^2) = \cos x^2 + i \sin x^2$, and then comparing both-hand sides with each other. This formal procedure is available for many other definite integrals.

APPENDIX IV

The 3N-dimensional hypervolume integral of the type given by

$$\int_{\infty} d^{3N}\vec{y}\; e^{-\alpha\beta y^2 + i\vec{y}\cdot\vec{c}} \prod_{j=1}^{n} (\vec{y}\cdot\vec{a}_j)$$

with the 3N-dimensional real vectors $\vec{y}$, $\vec{c}$, and $\vec{a}_j (j=1,2,3,\ldots,n)$ can be reduced to a linear combination of the types of the following 3N-cimensional hyper-volume integral:

$$J \overset{\text{def}}{=\!=} \int_{\infty} d^{3N}\vec{x}\; e^{-\alpha\beta\vec{x}^2} \prod_{\lambda=1}^{3N} x_\lambda^{n_\lambda} \tag{1}$$

by performing a transformation of the variable of integration given by

$$\vec{y} = \vec{x} - i\vec{c}/(2\alpha\beta) \; .$$

The new limit of integration is, therefore, $\infty + i\vec{c}/(2\alpha\beta)$, or $\infty(1+i\vec{c}/2\alpha\beta\infty)$, or ∞, i.e. the same as that of the old variable $\vec{y}$. Now, the integral J given by Eq. (1) can be split into the product of one-dimensional integrals of 3N in number, i.e.

$$J \equiv \prod_{\lambda=1}^{3N} J_\lambda, \quad J_\lambda \overset{\text{def}}{=\!=} \int_{-\infty}^{\infty} dz\; e^{-\alpha\beta z^2} z^{n_\lambda} \; . \tag{2}$$

Furthermore, the one-dimensional integral J_λ is changed into the Euler's Γ-function, i.e.

$$J_\lambda = (\sqrt{\alpha\beta})^{-(n_\lambda+1)} \int_0^{\infty} dt\; e^{-t} t^{(n_\lambda-1)/2} \sum_{j=0}^{\infty} \delta(n_\lambda, 2j), \tag{3}$$

by making a change of the variable of integration given by $t = \alpha\beta z^2$.

The combination of Eq. (3) with Eq. (2) gives

$$J = (\sqrt{\alpha\beta})^{-3N} \cdot \sum_{\lambda=1}^{3N} n_\lambda \cdot \prod_{\lambda=1}^{3N} \Gamma(\frac{n_\lambda+1}{2}) \cdot \sum_{j=0}^{\infty} \delta(n_\lambda, 2j),$$

where

$$\int_0^\infty dt\, e^{-t} t^{(n_\lambda-1)/2} \equiv \Gamma(\frac{n_\lambda+1}{2}) \cdot = \begin{cases} n_\lambda! \sqrt{\pi}/2^{n_\lambda} \cdot (n_\lambda/2)!, & (n_\lambda = 2j), \\ (\frac{n_\lambda-1}{2})!, & (n_\lambda = 2j+1) \end{cases} .$$

For example,

$$\int_\infty d^{3N}\vec{x}\, e^{-\alpha\beta\vec{x}^2} (\vec{a}\cdot\vec{x})^n \equiv (\frac{\pi}{\alpha\beta})^{3N/2} \cdot \frac{(\sqrt{\alpha\beta})^{-n} \cdot n!}{2^n \cdot (n/2)!} \cdot (\vec{a}^2)^{n/2} \cdot \sum_{j=0}^{\infty} \delta(n, 2j).$$

APPENDIX V

The Cayley-Hamilton's Theorem:

Since many authors have proved this theorem somewhat in their complex ways, we present here a simple and lucid way of proving it. We rewrite here Eq. (282) again.

$$\det(M-yI)_{-} \equiv \sum_{\lambda=0}^{N} c_{N-\lambda} y^{\lambda}, \tag{1}$$

and put $y = m_j$ in both-hand sides of this characteristic determinant by taking an eigenvalue m_j of the matrix M among its N eigenvalues $m_\mu(\mu=1,2,\ldots,j,\ldots,N)$, all of which satisfy the following characteristic equation with the unknown m:

$$\det(M-mI)_{-} = 0. \tag{2}$$

We have, then,

$$\sum_{\lambda=0}^{N} c_{N-\lambda} m_j^{\lambda} = 0. \tag{3}$$

Now, we construct a matrix polynomial with respect to the matrix M by using the coefficients $c_\lambda(\lambda=0,1,2,\ldots,N)$, i.e.

$$\sum_{\lambda=0}^{N} c_{N-\lambda} M^{\lambda}, \tag{4}$$

and apply an arbitrary N-dimensional vector $\vec{q}$ to the matrix-operator of Eq. (4) to have

$$\left(\sum_{\lambda=0}^{N} c_{N-\lambda} M^{\lambda}\right)\vec{q} = \sum_{\lambda=0}^{N} c_{N-\lambda}(M^{\lambda}\vec{q}). \tag{5}$$

We expand the vector $\vec{q}$ in terms of the N normalized eigenvectors $\vec{u}_j (j=1,2,3,\ldots,N)$ of the matrix M:

$$M\vec{u}_j = m_j \vec{u}_j, \tag{6}$$

to obtain in the following form:

$$\vec{q} = \sum_{j=1}^{N} a_j \vec{u}_j, \tag{7}$$

where the expansion coefficients $a_j (j=1,2,3,\ldots,N)$ are determined by the following simultaneous algebraic equation of first order:

$$\sum_{j=1}^{N} (\vec{u}_i \cdot \vec{u}_j) a_j = \vec{u}_i \cdot \vec{q}, \quad (i=1,2,3,\ldots,N). \tag{8}$$

We note here that we have, in our discussion, not assumed the Hermitian property of the matrix M as in quantum mechanics. Equation (7) is still valid even for our present case. Since $M \neq \tilde{M}$, $(\vec{u}_i \cdot \vec{u}_j)$ does not become the Kronecker's δ_{ij}. The linear independence of the N eigenvectors $\vec{u}_j (j=1,2,3,\ldots,N)$ can be proven easily. This fact guarantees the correctness of the expansion of Eq. (7). The substitution of Eq. (7) into the right-hand side of Eq. (5) gives

$$\begin{aligned}\left(\sum_{\lambda=0}^{N} c_{N-\lambda} M^{\lambda}\right)\vec{q} &= \sum_{j=1}^{N} a_j \sum_{\lambda=0}^{N} c_{N-\lambda}(M^{\lambda}\vec{u}_j) \\ &= \sum_{j=1}^{N} a_j \left(\sum_{\lambda=0}^{N} c_{N-\lambda} m_j^{\lambda}\right)\vec{u}_j \quad (\because \text{Eq. (6)}) \\ &= 0 \qquad (\because \text{Eq. (3)}),\end{aligned}$$

or

$$\sum_{\lambda=0}^{N} c_{N-\lambda} M^{\lambda} = 0,$$

since the vector $\vec{q}$ has been taken arbitrarily. Next, we put $y = 0$ in Eq. (1). We obtain then,

$$\det(M)_{-} = c_N.$$

We have, thus, proved the Cayley-Hamilton's theorem. The determination of the explicit form of Eq. (289) can be done as follows: Let us rewrite the recurrence formula of Eq. (287) in the following alternative form:

$$\left.\begin{aligned} Nc_1 &= (-1)^{N+1} x_1 , \\ \sum_{j=1}^{\lambda-1} \binom{N-j}{\lambda-j} x_{\lambda-j} c_j + Nc_\lambda &= (-1)^{N+1} \binom{N}{\lambda} x_\lambda \\ (\lambda &= 2,3,4,\ldots,N), \end{aligned}\right\} \tag{9}$$

where we have used a notation defined by

$$\binom{N}{i} \overset{\text{def}}{=\!=} N! \div \left\{ i! \cdot (N-i)! \right\} .$$

Equation (9) is a simultaneous algebraic equation of first order with N unknowns $c_j (j=1,2,3,\ldots,N)$. We can, therefore, find all the unknowns $c_j (j=1,2,3,\ldots,N)$ in their determinantal form by using an elementary method. For example, the unknown c_N is as follows:

$$\det(M)_{-} = c_N = \Delta_N' \div \Delta \tag{10}$$

where

$$\Delta \equiv \begin{vmatrix} N & 0 & 0 & 0 \ldots\ldots 0 & 0 & 0 \\ \binom{N-1}{1}x_1 & N & 0 & 0 \ldots\ldots 0 & 0 & 0 \\ \binom{N-1}{2}x_2 & \binom{N-2}{1}x_1 & N & 0 \ldots\ldots 0 & 0 & 0 \\ \binom{N-1}{3}x_3 & \binom{N-2}{2}x_2 & \binom{N-3}{1}x_1 & N \ldots\ldots 0 & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \binom{N-1}{N-2}x_{N-2} & \binom{N-2}{N-3}x_{N-3} & \binom{N-3}{N-4}x_{N-4} \cdots\cdots \binom{2}{1}x_1 & N & 0 \\ \binom{N-1}{N-1}x_{N-1} & \binom{N-2}{N-2}x_{N-2} & \binom{N-3}{N-3}x_{N-3} \cdots\cdots \binom{2}{2}x_2 & \binom{1}{1}x_1 & N \end{vmatrix} = N^N$$

and

$$\Delta'_N \equiv \begin{vmatrix} \binom{N}{1}x_1 & N & 0 & 0 \ldots\ldots 0 & 0 & 0 \\ \binom{N}{2}x_2 & \binom{N-1}{1}x_1 & N & 0 \ldots\ldots 0 & 0 & 0 \\ \binom{N}{3}x_3 & \binom{N-1}{2}x_2 & \binom{N-2}{1}x_1 & N \ldots\ldots 0 & 0 & 0 \\ \binom{N}{4}x_4 & \binom{N-1}{3}x_3 & \binom{N-2}{2}x_2 & \binom{N-3}{1}x_1 \ldots\ldots 0 & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \binom{N}{N-2}x_{N-2} & \binom{N-1}{N-3}x_{N-3} & \binom{N-2}{N-4}x_{N-4} & \binom{N-3}{N-5}x_{N-5} \cdots \binom{3}{1}x_1 & N & 0 \\ \binom{N}{N-1}x_{N-1} & \binom{N-1}{N-2}x_{N-2} & \binom{N-2}{N-3}x_{N-3} & \binom{N-3}{N-4}x_{N-4} \cdots \binom{3}{2}x_2 & \binom{2}{1}x_1 & N \\ \binom{N}{N}x_N & \binom{N-1}{N-1}x_{N-1} & \binom{N-2}{N-2}x_{N-2} & \binom{N-3}{N-3}x_{N-3} \cdots \binom{3}{3}x_3 & \binom{2}{2}x_2 & \binom{1}{1}x_1 \end{vmatrix} \quad (11)$$

We remember here again the following definition:

$$x_j \overset{\text{def.}}{=\!=} \mathrm{Tr}(M^j)_-, \quad (j=1,2,3,\ldots,N).$$

In this way, we can determine $\det(M)_-$ as a polynomial of N order with respect to the N traces x_j (j=1,2,3,...,N) by expanding only the determinant Δ'_N given by Eq. (11). As known from Eq. (11), this polynomial is N order in x_1, (N-1) order in x_2, (N-2) order in x_3,..., and first order in x_N. An interesting result happens if we take M = I (unit matrix) in Eq. (10). We have, then from Eqs. (10), (11), and $x_1 = x_2 = x_3 = \ldots = x_N = N$,

$$\begin{vmatrix}
\binom{N}{1} & 1 & 0 & 0 & \ldots\ldots & 0 & 0 & 0 \\
\binom{N}{2} & \binom{N-1}{1} & 1 & 0 & \ldots\ldots & 0 & 0 & 0 \\
\binom{N}{3} & \binom{N-1}{2} & \binom{N-2}{1} & 1 & \ldots\ldots & 0 & 0 & 0 \\
\binom{N}{4} & \binom{N-1}{3} & \binom{N-2}{2} & \binom{N-3}{1} & \ldots\ldots & 0 & 0 & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\binom{N}{N-2} & \binom{N-1}{N-3} & \binom{N-2}{N-4} & \binom{N-3}{N-5} & \ldots\ldots & \binom{3}{1} & 1 & 0 \\
\binom{N}{N-1} & \binom{N-1}{N-2} & \binom{N-2}{N-3} & \binom{N-3}{N-4} & \ldots\ldots & \binom{3}{2} & \binom{2}{1} & 1 \\
\binom{N}{N} & \binom{N-1}{N-1} & \binom{N-2}{N-2} & \binom{N-3}{N-3} & \ldots\ldots & \binom{3}{3} & \binom{2}{2} & \binom{1}{1}
\end{vmatrix}_- = 1 \qquad (12)$$

This relation of Eq. (12) makes us know that the first term of the expansion of Eq. (10) is unity. This is in agreement with our expectation obtained simply from Eq. (280). As shown in Eq. (290), every trace contains the particle number N in its function form, i.e. in

general, in an appropriate notations,

$$\mathrm{Tr}(M^j)_- \equiv \left[\prod_{s=1}^{j}\sum_{\lambda(s)=1}^{N}\right]\left[1 - \prod_{s=1}^{j}\delta_{\lambda(s),\lambda(s+1)}\right]$$

$$\cdot \exp\left[-\frac{q}{2}\sum_{s=1}^{j}\left(\vec{r}_{\lambda(s)} - \vec{r}_{\lambda(s+1)}\right)^2\right] + N,$$

where $\lambda(j+1) \equiv \lambda(1)$. The meaning of these notations can be understood easily. This constant N contained in every trace forms together the determinant of Eq. (12) multiplied by the number N^N. If we want to find the numerical coefficient of $x_2 \equiv \mathrm{Tr}(M^2)$, it is better to have such a procedure that we put, at first, $x_j = 0$ $(j=3,4,\ldots,N)$ in Eq. (11), and, then, differentiate the determinant so obtained with respect to x_2 to obtain the value of the differential quotient at $x_2 = 0$. This value gives, then, the coefficient in question.

LIST OF REFERENCES

1. M. Born; Zeits. f. physik, 37, 863 (1926).

2. D. ter Haar; Rev. Mod. Phys. 27, 289 (1955).

3. U. Fano; Rev. Mod. Phys. 29, 74 (1957).

4. R. McWeeny; Rev. Mod. Phys. 32, 335 (1960).

5. P. S. Hubbard; Rev. Mod. Phys. 33, 249 (1961).

6. K. Z. Husimi; Proc. Phys.– Math. Soc. Japan, 22, 264 (1940).

7. "Some Notes on the Density Operator by using Dirac's ket-bra Description" by the author of this paper (unpublished).

8. V. M. Fain; Soviet Physics, Uspekhi, 6, 294 (1963).

9. M. Fuzihara; Mathematical Analysis, Vol. 2, Chapter 6, Tokyo, Japan (1952).

10. J. K. Jaen; General Mechanics, Chapter 4, Seoul, Korea (1956).

11. J. Von Neumann; Mathematishe Grundlagen der Quantenmechanik, Kapitel 3 et. seq. (1932).

12. P.A.M. Dirac; The Principles of Quantum Mechanics, 3rd Edition, P 132 et seq. (1947).

13. R. C. Tolman; The principles of Statistical Mechanics, Chapter X, Oxford Univ. Press, (1950). See also Appendix VIII.

14. J. C. Slater; Phys. Rev. 38, 237 (1931).

15. F. Bloch; Z. Physik 74, 295 (1932).

16. E.G.D. Cohen; Fundamental Problems in Statistical Mechanics, loc. cit., Interscience Publisher, New York (1962).

17. K. Z. Husimi; Quantum Statistical Mechanics, Part B, Chapter 1, Kyoritsu Publisher, Tokyo, Japan (1953).

18. H. Weyl; Gruppentheorie und Quantenmechanik, V. Kaptel, Sec. 9, S. Hirzel Verlag, Leipzig (1928); translated version, "Theory of Groups and Quantum Mechanics" Dover, New York (1950).

19. S. S. Schweber; An Introduction to Relativistic Quantum Field Theory, Part Two, Chapter 6, Row, Peterson and Company, Evanston, Illinois (1961).

20. A. A. Broyles; Lecture Book in Quantum Mechanics, University of Florida (unpublished) (1962).

21. J. S. Lomont; Applications of Finite Groups, Chapter VII, Academic Press, New York (1959).

22. Hardy-Ramanujan; Proc. London Math. Soc. (2), 17, 75 (1918).

23. Rademmacher; Proc. London Math. Soc. (2), 43, 241 (1937).

24. B. Kahn and G. E. Uhlenbeck; Physica, 5, 399 (1938).

25. F. Lado; Phys. Rev. 135, 1013 (1964).

26. L. D. Landau and E. M. Lifshitz; Statistical Physics, Sec. 33, Translated by E. Peierls and R. F. Peierls, Addison-Wesley Publishing Co., Inc. (1958).

27. J. Kirkwood; Phys. Rev. 44, 31 (1933).

28. G. E.Uhlenbeck and E. Beth; Physica, 3, 729 (1936).

29. G. E. Uhlenbeck and E. Beth; Physica, 4, 915 (1937).

30. J. de Boer; Contribution to the Theory of Compressed Gases, Dissertation, University of Amsterdam (1940).

31. J. de Boer; Rep. on Progress in Physics, 12, 305 (1948).

32. K. Z. Husimi; Proc. Phys.— Math. Soc., Japan, 22, 264, Part I, Sec. 7 (1940).

33. J. E. Mayer and W. Band; J. Chem. Phys. 15, 141 (1947).

34. D. ter Haar; Elements of Statistical Mechanics, Chapter 8 (1954).

35. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird; Molecular Theory of Gases and Liquids, P 437, Problem 1, John Wiley and Sons, Inc., New York (1964).

36. K. Huang; Statistical Mechanics, P.149, John Wiley and Sons, Inc. (1963).

37. K. Terazawa; Mathematical Analysis for Scientists, Vol. 1, P 221 et seq., Iwanami Publisher, Tokyo, Japan (1955).

38. F. Zernicke and I Prins; Z. Phys., 41, 184 (1927).

39. J. G. Kirkwood; J. Chem. Phys. 3, 300 (1935).

40. J. G. Kirkwood; Chem. Rev. 19, 275 (1936).

41. A. A. Broyles; J. Chem. Phys 34, 359 (1961).

42. J. G. Kirkwood, E. K. Maun and B. J. Alder; J. Chem. Phys. 18, 1040 (1950).

43. A. G. McLellan; Proc. Soc. (London), A210, 509 (1952).

44. M. Born and H. S. Green; Proc. Roy. Soc. (London); A188, 10 (1946).

45. N. N. Bogolyubov; Problems of Dynamical Theory in Statistical Physics, (Russian) State Technical Press (1946).

46. J. Yvon; "Actualités scientifiques et industrielles", P 203, Herman and Cie, Paris (1935).

47. H. S. Green; Proc. Roy. Soc. (London), A189, 109 (1947).

48. A. Eisenstein and N. Gingrich; Phys. Rev. 62, 261 (1942).

49. A. Michels and H. Wijker; Physica, 15, 627 (1949).

50. J. Kirkwood; Discussions Faraday Soc., 15, 35 (1953).

51. L. Sarolea and J. Mayer; Phys. Rev. 101, 1627 (1956).

52. R. Abe; Progr. Theor. Phys. (Kyoto) Japan, 21, 421 (1959).

53. A. Richardson; J. Chem. Phys. 23, 2304 (1956).

54. G. H. A. Cole; Adv. Phys. 8, 225 (1959).

55. I. Z. Fisher; Soviet Phys.— Uspekhi, 5, 239 (1962).

56. D. Bohm and D. Pines; Phys. Rev. 85, 338 (1952).

57. J. K. Percus and G. J. Yevick; Phys. Rev. 110, 1 (1958).

58. J. K. Percus; Phys. Rev. Letters 8, 462 (1962).

59. J. L. Lebowitz and J. K. Percus; J. Math. Phys. 4, 116 (1963).

60. J. Yvon; Nuovo Cimento 9, 144 (1958).

61. H. D. Ursell; Proc. Cambridge Phil. Soc. 23, 685 (1927).

62. J. E. Mayer and S. F. Harrison; J. Chem. Phys. 6, 87 (1938).

63. M. Born and K. Fuchs; Proc. Roy. Soc. A166, 391 (1938).

64. J. E. Mayer and E. W. Motroll; J. Chem. Phys. 9, 2 (1941).

65. E. E. Salpeter; Ann. Phys. (N. Y.); 5, 183 (1958).

66. J. M. J. Van Leeuwen, J. Groeneveld, and J. de Boer; Physica, 65, 792 (1959).

67. E. Meeron; J. Math. Phys. 1, 192 (1960).

68. T. Morita and K. Hiroike; Progr. Theoret. Phys., (Kyoto) Japan, 23, 1003 (1960).

69. M. S. Green; technical report, Hughes Aircraft Corp. (unpublished).

70. G. S. Rushbrooke; Physica, 26, 259 (1960).

71. L. Verlet; Nuovo Cimento, 18, 77 (1960).

72. Max Klein and M. S. Green; J. Chem. Phys. 39, 1367 (1963).

73. L. S. Ornstein and F. Zernicke; Proc. Acad. Sci. Amsterdam, 17, 793 (1914).

74. G. Stell; Physica, 29, 517 (1963).

75. F. Lado; The doctoral dissertation, University of Florida, Gainesville, Florida (1964).

76. S. A. Rice and P. Gray; The supplement in the translated version of the Russian book titled "Statistical Theory of Liquids" by Fisher, P 296 et seq., University of Chicago Press (1964).

77. E. Helfand and R. L. Kornegay; Physica, 8, 1481 (1964).

78. L. Verlet; Physica, 31, 959 (1965).

79. J. L. Lebowitz; Phys. Rev. 133, 895 (1964).

80. J. L. Lebowitz and E. Praestgaard; J. Chem. Phys. 40, 2951 (1964).

81. H. L. Frisch and J. L. Lebowitz; The Equilibrium Theory of Classical Fluids, Section II, P 171 et seq., W. A. Benjamin, Inc., New York (1964).

82. V. Volterra; Theory of Functionals and of integral and integro-differential equations, Dover, New York (1959).

83. R. H. Fowler and E. A. Guggenheim; Statistical Thermodynamics, P 390, Cambridge University Press (1939).

84. J. G. Kirkwood and Z. Salsburg; Discussions Faraday Soc., 15, 28 (1953).

85. A. A. Broyles; J. Chem. Phys. 33, 456 (1960).

86. A. A. Broyles; J. Chem. Phys. 34, 359 (1961).

87. A. A. Broyles; J. Chem. Phys. 34, 1068 (1961).

88. A. A. Broyles; J. Chem. Phys. 35, 493 (1961).

89. A. A. Broyles, S. U. Chung, and H. L. Sahlin; J. Chem. Phys 37, 2462 (1962).

90. A. A. Broyles, H. L. Sahlin, and D. D. Carley; Phys. Rev. Letters, Vol. 10, No. 8, 319 (1963).

91. C. C. Carley; Phys. Rev. 131, 1406 (1963).

92. A. A. Khan; Phys. Rev. 134, 367 (1964).

93. F. Lado; Phys. Rev. 135, 1013 (1964).

94. D. D. Carley; Phys. Rev. 136, 127 (1964).

95. A. A. Khan; Phys. Rev. 136, 1260 (1964).

96. M. Klein and M. S. Green; J. Chem. Phys. 39, 1367 (1963).

97. A. Michels and others; Physica, 26, 381 (1960).

98. N. Kestner and O. Sinanoglu; J. Chem. Phys. 38, 1730 (1963).

99. M. S. Wertheim; Phys. Rev. Letters 10, 321 (1963).

100. E. Thiele; J. Chem. Phys. 38, 1959 (1963).

101. E. Feenberg; J. Math Phys. 6, 658 (1965).

102. C. Kittel; Quantum Theory of Solids, Chapter 19, John Wiley and Sons, Inc., New York (1963), et al.

103. L. Van Hove; Phys. Rev., 95, 249 (1954).

104. L. Brillouin; J. Appl. Phys., 20, 1110 (1949).

105. A. A. Khan and A. A. Broyles; J. Chem. Phys., 43, 43 (1965).

106. A. A. Khan; Interatomic Potentials of Krypton and Argon, University of Florida, Gainesville, Florida (unpublished).

107. A. A. Khan and A. A. Broyles; Phys. Rev., 139, 1805 (1965).

108. Strominger, Hollinger, and Seaborg; Table of Isotopes, Revs. Modern Phys., 30, 585 (1958).

109. Suess and Urey; Abundances of the elements, Revs. Modern Phys., 28, 53 (1956).

110. R. H. Fowler; Statistical Mechanics, Cambridge University Press, 2nd ed., P 295 (1936).

111. T. Kihara; Rev. Modern Phys., 25, 831 (1953).

112. J. E. and M. F. Kilpatrick; J. Chem. Phys., 19, 930 (1951).

113. T. Kihara; Rev. Modern Phys., 27, 412 (1955).

114. Bird, Spots, and Hirschfelder; J. Chem. Phys., 18, 1395 (1950).

115. DuMond et al.; Revs. Modern Phys., 27, 363 (1955).

116. J. S. Rowlinson; Ann. Reports of the Chem. Soc. London, 56, 22, (1959).

117. R. A. Buckingham and J. Corner; Proc. Roy. Soc. London, A189, 118 (1947).

118. W. E. Rice and J. O. Hirschfelder; J. Chem. Phys., 22, 187 (1954).

119. E. A. Mason and W. E. Rice; J. Chem. Phys., 22, 522, 843 (1954).

120. A. A. Khan; Doctoral Dissertation, Chapter V, University of Florida, Florida (1963).

121. D. Stirpe and C. W. Tompson; J. Chem. Phys., 36, 392 (1962).

122. A. A. Khan; Radial Distribution Functions of Liquid Neon, University of Florida, Florida (1964) (unpublished).

BIOGRAPHICAL SKETCH

Jong Kook Jaen was born in Songjin, Hamkyongbook-do, North Korea, on July 19, 1925. Upon graduation from Likkyo High School, Tokyo, Japan, he entered the Department of Science, Sizuoka Junior College (now called Sizuoka University), Sizuoka, Japan, and graduated from that college in March, 1945. After graduation, he went back to his native town in order to escape from the danger of bombardment from B-29 U. S. bombers in accordance with his parents instructions. From 1945 to 1947, he taught physics and mathematics at the Junior Engineering College in his native town. During that time, he joined an underground organization for fighting the communist party of North Korea. Since the communist police started to arrest all members of that organization, he fled from North Korea with his idealogical friends to come to Seoul, South Korea. He entered Hanyang University (called Hanyang Institute of Technology at that time) and received the degree of Bachelor of Electrical Engineering in March, 1952. After receiving that degree, he was appointed as a member of the faculty at that university. He worked there not only in teaching physics and mathematics for eight years but also having the administrative positions such as the Director of the school of common basic courses, the Acting Director of Academic Affairs, the Chairman of the Department of Physics and Mathematics until August, 1960. In September 1960, he started graduate study of physics at Auburn University, Auburn, Alabama, and

received the degree of Master of Science in Physics in August, 1961. He transferred to the University of Florida, Gainesville, Florida to go on with his graduate study leading to the degree of Doctor of Philosophy in Physics on September of 1961, and studied for one year until June, 1962. He went back to his home university in Seoul, Korea, under the instruction of the president of that university, and then worked there not only in teaching the graduate students of physics but also holding the administrative position of the director of the experimental facilities for two years until he returned again to the University of Florida to continue his graduate study on September, 1964. He is holding still the position of the Professor of Physics at his home university, and the author of the following first five books written in Korean and the translater (with his co-translators) of the following latter five American books translated into Korean: (1) General Mechanics (pp 511), (2) Introduction to Applied Analysis (pp 540), (3) Theory of Relativity (pp 320), (4) Tensor Analysis (pp 200), and (5) Mathematics for Physicist and Engineer (pp 302); also (a) Analytical Experimental Physics by Lemon, (b) Engineering Mechanics by Merrian, (c) Physical Mechanics by Symon, (d) Physics for Engineer and Physicist by Follower, and (e) Laboratory Physics by Teller.

He married Jung Im Lee in September, 1953, and is the father of one girl and two sons.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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